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of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIV MAY 1959 No. 5

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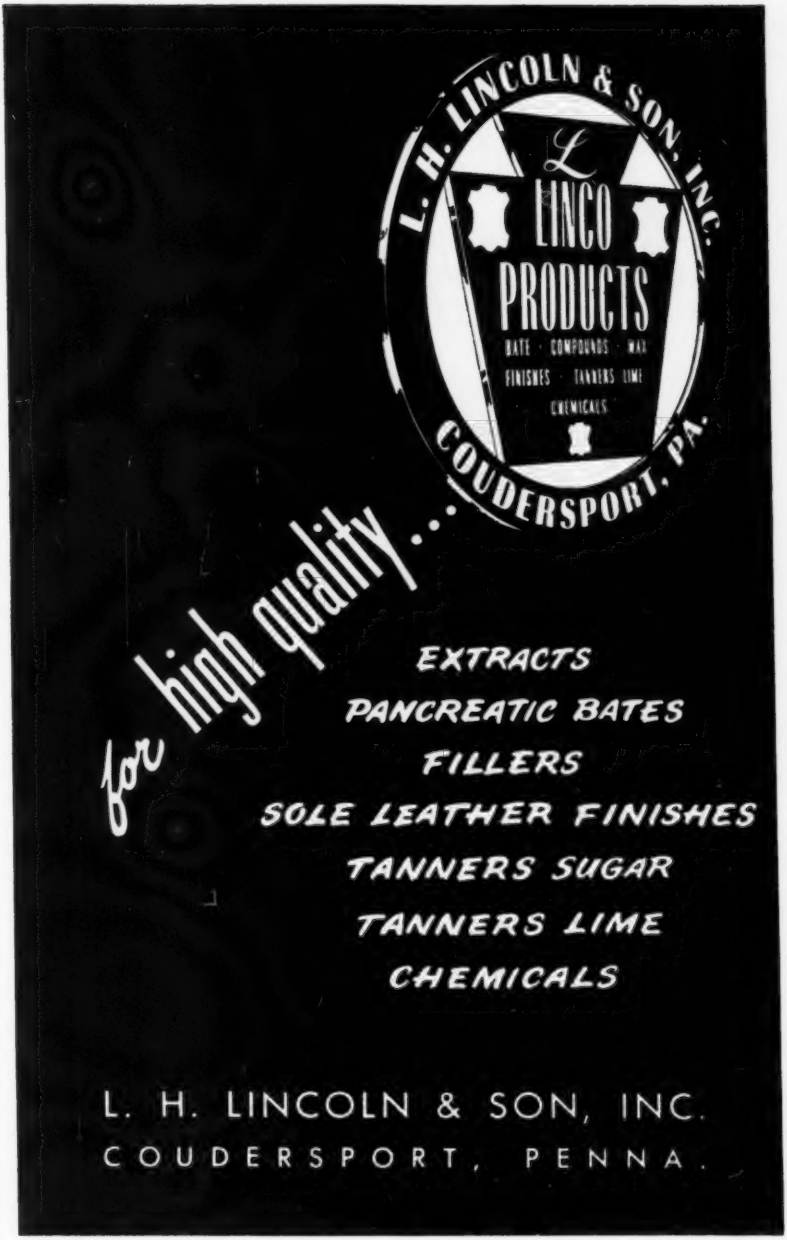
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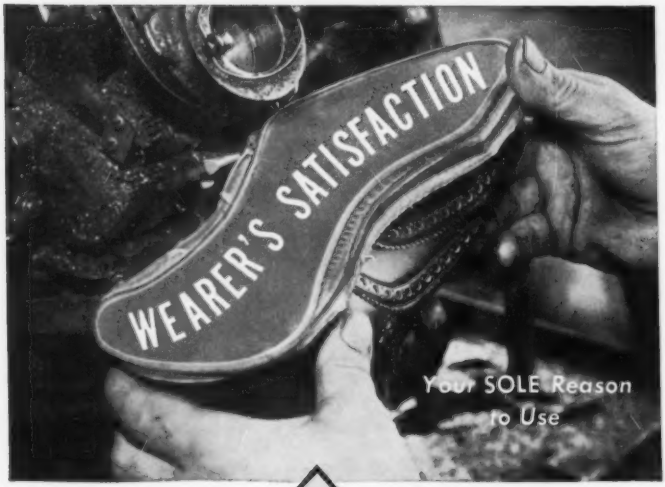

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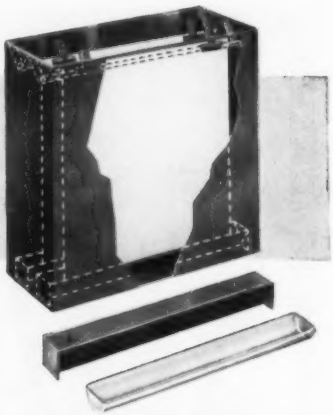

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SOME NOTES ON THE PROBLEM OF THE PREPARATION OF PURE FIBROUS COLLAGEN

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INTRODUCTION

In much work that is of interest to the leather chemist the properties of fibrous collagen, the protein that is the chief component of the skin, are of importance. Therefore it is useful, and in some work essential, to use a fibrous collagen preparation which is as pure as possible in order to study these properties. Since fibrous collagen is a protein which is insoluble in most solvents and dissolves only in those solvents in which it is probable that some degradation occurs, its purification is much more difficult than that of most proteins, which can be purified by repeated solution and precipitation.

The present paper will assess the problem of purification from two points of view: (*a*) the components of the skin other than fibrous collagen which must be removed in the purification, and (*b*) the methods of purification which have been used up to the present time. It should always be borne in mind that a method of purification is not necessarily successful if it has removed all the other foreign matter; it should also leave the fibrous collagen in the undegraded or native state.

COMPONENTS OF SKIN

Since fibrous collagen is insoluble in aqueous solutions, it is purified by extracting the other skin constituents. The nature of all these other components which must be removed has not been established. In this section data obtained by a number of investigators on the quantitative composition of skin will be given.

Globular proteins.—The globular proteins include albumin and globulins of the blood serum and lymph. Tancous (18), using her method of protein fractionation of bovine skin, reported that 6.4% of the total nitrogen of whole heavy steerhide was globular protein nitrogen. These globular proteins were characterized by precipitation with 3% trichloracetic acid. In calfskin the amount was larger (10.9%).

Since albumin and globulins are soluble in dilute salt solutions, one measure of the minimum amount of these proteins present in the skin may be obtained from a study of the salt extracts, although there is probably also present in

*Ernest Griess Fellow

the extracts a small amount of salt-soluble collagen (8, 33). Kritzinger (21) found that approximately 1.5% of the total hide nitrogen was protein nitrogen that could be extracted by shaking with 10% sodium chloride solution at 25°C. for 24 hr.; approximately half this amount of nonprotein nitrogen was simultaneously extracted. The amount of nitrogen extracted increased with time, but even after 168 hr. it had not reached a maximum. However, there was evidence of bacterial or autolytic attack on the collagen before this time.

Using the corium of bovine hide (an old animal was chosen because it would have a minimum of ground substance), Schmitt, Gross, and Highberger (33) found that only 1% of the total dry protein of the corium was extracted in 11 extractions with 10% sodium chloride solution. The smaller amount of salt-extractable protein found in this experiment is probably a result of the fact that corium, and not whole hide, was used and that the hide was from an old animal.

Mucoids and glycoproteins.—Mucoids and glycoproteins, the carbohydrate-containing conjugated proteins of hide, are presumably associated with the ground substance in which the collagen fibers are embedded.

DeBeukelaer and Marbach (11), working with ground whole hide from which most of the albumin and globulins had been previously removed by 2 extractions with 10% sodium chloride solution, found that 1% of the total nitrogen of the hide could be extracted with half-saturated calcium hydroxide solution; presumably this nitrogen is the nitrogen of mucoids and glycoproteins.

In addition to mucoids and glycoproteins collagen fibers themselves seem to be soluble in half-saturated calcium hydroxide, if the extractions are sufficiently prolonged (33).

Reticulin.—The question of the existence of reticulin as an entity distinct from fibrous collagen is apparently being answered in the negative on the basis of present research. Küntzel (22), in a recent review article, has stated very clearly the case against the existence of reticulin in skin. The English school (4) regards reticulin as composed of a protein part, which is entirely collagen, associated with 4% carbohydrate and 10 to 12% bound lipid.

Elastin and keratin.—The problem of elastin is also in a state of flux. Tancous (18), using a method based on the insolubility of elastin and keratin in hot 0.1% hydrochloric acid, reported that 4.5% of the total nitrogen of heavy steerhide was elastin and keratin nitrogen; the figure was 12.7% for calfskin. DeBeukelaer and Marbach (11), using a similar method, found that 3.85% of the total nitrogen of fresh hide is elastin and keratin. The insoluble residue remaining after autoclaving has also been considered to be elastin (25). Bowes (4) reports that this fraction is 0.6% of the protein of whole skin; Roddy (32) found it to be somewhat larger, approximately 1%.

Burton's recent work (6), however, has thrown some doubt on the independent existence of elastin as a protein entirely distinct from fibrous collagen. When fibrous collagen is treated with borate buffers (pH 7 to 10.4), it gives rise to material closely resembling elastin; this transformation could also be brought about by proteolytic enzymes or by sodium metaperiodate. The question of the chemical changes which the collagen has undergone is one that demands further study.

Since keratin occurs only in the epidermis, it is mechanically removed if only the corium split is used for the collagen preparation.

Soluble collagens.—The question of the nature and number of the soluble collagens or "procollagens" that are present in the skin has still to be brought into some kind of order. There are essentially 4 points of view at the present time: (*a*) the soluble collagens are a few distinct entities (the acid citrate-soluble collagen, the alkaline buffer-soluble collagen, and the neutral salt-soluble collagen), one or more of which are probably precursors of fibrous collagen; (*b*) the Orekhovitch theory that citrate-soluble collagen or "procollagen" is the biological precursor of fibrous collagen, existing in the skin in a number of "transient" forms of which alkaline buffer-soluble collagen and neutral salt-soluble collagen are two; "procollagen" and the "tropocollagen" of Highberger are identical (29); (*c*) the soluble collagens are a continuous series of collagens of decreasing solubility, of which acid-soluble collagen and neutral salt-soluble collagen are two arbitrary fractions (12); and (*d*) a portion at least of the acid citrate-soluble collagen is derived from the fibrous collagen (33).

At the present time the evidence is not sufficient to serve as a basis for a decision between these viewpoints.

Alkaline buffer-soluble collagen.—Neuberger (27), working with young rabbit skin, found that the neutral- or alkali-soluble collagen constitutes 4% of the total collagen. On the basis of isotope experiments he regards this material, and not the acid-soluble collagen, as the precursor of fibrous collagen. However, in the process of purification after isolation the alkaline buffer-soluble collagen lost its solubility at neutral or slightly alkaline pH, and when finally purified, it resembled the acid-soluble collagen in all the properties examined. This easy convertibility of the alkali-soluble to the acid-soluble collagen suggests a very close similarity in chemical composition. Whether this conversion is a property of the soluble collagens of skins of other species is yet to be determined.

Young calfskin contains more alkali-soluble collagen than old skin (13).

Acid citrate-soluble collagen.—Orekhovitch (29) has made extensive studies of the acid citrate-soluble collagen of skins of a number of species. He reports the presence of large amounts in young guinea pig skin (7 to 10%) and

much less in the skin of older guinea pigs (less than 1%). In calfskin he found that acid citrate-soluble collagen was only 0.86% of the skin on a dry-weight basis.

Bowes, Elliott, and Moss (4) reported that calfskin which had been ground in the Wiley mill and then extracted with alkaline phosphate at pH 8.6 lost approximately 5% of its total protein (on the basis of total nitrogen) on 4 extractions with 0.12*M* citrate (pH 3.6). If only the corium split was used, and if this was sectioned with a freezing microtome and then extracted with phosphate, approximately 20% of the total nitrogen was removed by 7 citrate extractions. The soluble proteins obtained in these 2 experiments were found by hydroxyproline determination to be over 90% collagen.

The larger amounts of collagen which were solubilized in the second experiment may be due to the fact that the sectioned pieces were stored in phosphate buffer at pH 9 until the sectioning was complete. Courts (10) has shown that if collagenous tissue undergoes a cold alkaline soak, substantial percentages of the collagen can be solubilized with 0.1*M* citric acid as solvent. This effect may therefore be evident in the Bowes experiment.

Recent evidence has been gathered that appears to be in support of the view that the citrate-soluble collagen is very similar to, if not identical with, fibrous collagen. From the present analyses of citrate-soluble collagen (4) it is evident that on the basis of amino acid nitrogen as percentage of total nitrogen the citrate-soluble collagen has essentially the same amino acid composition as fibrous collagen, although the amide nitrogen, tyrosine, and histidine contents of the citrate-soluble collagen appear to be slightly lower, and the hydroxyproline content slightly higher. The citrate-soluble collagen, however, probably contains 4 to 5% of some nonprotein constituent.

Randall *et al.* (31) suggest that the chemical differences between the soluble collagen and the fibrous collagen may be akin to those observed for the albumin-plakalbumin transformation, in which albumin, a protein of molecular weight approximately 45,000, loses a small peptide by the action of an enzyme, thereby being converted into another protein, plakalbumin, of molecular weight approximately 44,700.

On the basis of physical data Veis and Cohen (35) postulate that the intact collagen fibers are networks of chains held together by acid-labile and acid-stable bonds, with unincorporated strands held in place by purely physical forces; the intact fibers are broken down by dilute acid at low temperature to give the soluble "procollagen".

Gross, Highberger, and Schmitt (13) have shown that, while a soluble collagen may exist in the ground substance and probably can be extracted by the mildest means (salt solution at or near neutral pH), a portion at least of the collagen extracted by acid citrate is derived from the formed fibrils of the corium. Part of the evidence on which this finding is based is electron microscopic examination of the extracted residue, which shows considerable

disorganization of the fibrils. They believe, then, that the "procollagen" of Orekhovitch represents not a biological precursor of collagen but a solution of the units (tropocollagen) of which the fibers are formed.

Mikhailov (26), in a study of young rat skin, found that 20% of the collagen was extracted by citrate buffer. The insoluble collagen remaining he called "kollastromin". According to Mikhailov this insoluble collagen did not show the striations or cross bonds seen in the electron microscope in normal collagen specimens, and the 2.9 A. spacing in the X-ray diagram normally associated with collagen was absent. Possibly the divergence between this work and that of the other investigators results from species differences in the skins used.

Nonprotein constituents.—In addition to its protein constituents skin contains nonprotein nitrogenous compounds, other organic compounds such as sugars, various inorganic salts, and lipids. The amount of lipid varies greatly with the hide within the same species. DeBeukelaer and Marbach (11) report 8.07% fat and 0.90% total ash in a fresh hide. Kritzinger (21) found that when cubed fresh hide was extracted with 10% sodium chloride solution by shaking for 24 hr. at room temperature, approximately 0.8% of the total hide nitrogen was extractable nonprotein nitrogen. This amount represents only the minimum amount of nonprotein nitrogen present in the hide, since continued extraction removed further small amounts of the material.

In the purification of fibrous collagen no specific measures are taken to remove the nonprotein water-soluble constituents or the salts, since they are considered to be extracted in the aqueous solutions used for removal of the soluble protein constituents. The lipids can be removed by various organic solvents.

METHODS OF PURIFICATION OF FIBROUS COLLAGEN

Prevention of bacterial action.—The hide should be protected from bacterial action from the time it is removed from the animal until the purification of the collagen is considered complete. However, the method by which this is to be attained poses some difficulties.

If the hide is frozen, difficulties may be encountered later in attempting to extract the soluble proteins from the hide, since it has been shown that the solubility of some of the proteins may be changed during the freezing process. Gross, Highberger, and Schmitt (13), for instance, have shown that if skin is frozen for more than a week, it yields very little salt-extractable collagen. Cooper and Sykes (9) found that fresh hide that has been freeze-dried does not rehydrate completely, unless, prior to the freeze-drying, it has been extracted with sodium chloride and then with lime solution. This fact suggests that the properties of the soluble proteins, but not of the fibrous collagen, have been affected by freeze-drying. Cooper (8) also found that the material

extracted from hide with 10% sodium chloride was completely soluble in phosphate-sodium chloride buffer at pH 7.3 before it was freeze-dried; but after freeze-drying some of the material was not soluble under these conditions. He believes that the serum proteins were not denatured by the freeze-drying but that it was other non-collagenous proteins and possibly mucopolysaccharides which were made insoluble.

In the purification of fibrous collagen, therefore, freezing of the hide for extended periods before the extractions are carried out should be avoided. However, bacterial action can be minimized by carrying out all the extractions in the cold (34).

A number of bactericidal agents, for example, Merthiolate or Roccal (an alkyl dimethylbenzyl ammonium chloride) may be added to the solutions at 1:10,000 dilution during the extractions to prevent bacterial action. The former cannot be used in acid solution (e.g., in citrate at pH 3). The useful effects of bactericides in minimizing bacterial action should be weighed against their possible harmful effects before they are used. They must not degrade or combine with the collagen. If the soluble fractions are to be studied, it should be remembered that the 100 mg. of bactericide per l. of extract may become an important impurity in the extracted material. If the bactericide is nitrogen-containing (for example, Roccal), its nitrogen contribution must be taken into consideration in any nitrogen distribution studies.

Methods of splitting and cubing.—Since fibrous collagen is usually prepared from the corium, the layer of hide which contains the least amount of non-collagenous proteins, it becomes necessary to remove the grain and flesh layers. When work is done on a small scale, it is possible to do this operation by hand; but for preparation of larger quantities of fibrous collagen the work is greatly facilitated if a splitting machine of the type used in the leather industry is used. In this case preliminary treatment of the hide is necessary so that the splitting may proceed satisfactorily. Three methods of preparation of the hide have been used. The first is freezing. While prolonged freezing is not desirable, it is probable that freezing for the short period necessary for the splitting will be satisfactory. Veis and Cohen (34) allowed the hide to swell in cold 2% acetic acid (pH 3 to 4) before splitting. A third type of treatment, used by Cassel and Kanagy (7), is partial dehydration of the hide, accomplished by an overnight soak in acetone.

After the corium split is obtained, it is usual to cube or to shred the corium before the extractions are started. In general, the smaller the corium pieces, the more thorough will be the extractions. However, it is known that fibrous collagen is more susceptible to enzyme action at a cut surface (2) and that the X-ray diffraction diagram is changed on grinding in a Wiley mill (17). These facts suggest that the question of degree of maceration should be given careful consideration.

Frequently the hide is cut into 1-cm. cubes. DeBeukelaer and Marbach (11) found evidence of collagen decomposition if a hide was shredded with dry ice in a hammer mill; but if the hide was first frozen in liquid nitrogen and then put through a Wiley mill with dry ice, decomposition appeared to be minimized. Shredding in a Wiley mill or other similar apparatus without providing for cooling to dissipate the heat which is always generated is, of course, to be avoided.

Treatment with trypsin.—In a number of methods for the preparation of purified fibrous collagen, corium was treated with trypsin to remove elastin, since it was thought that trypsin attacked elastin but not fibrous collagen. However, recent work has not supported the belief that a trypsin treatment is advisable in the purification of fibrous collagen. It has been found that crystalline trypsin does not attack elastin. Presumably the crude pancreatin previously used contained elastases, a group of enzymes which attack elastin. The whole question of the action of these enzymes is now an active field of study (1).

Another question which is still very much undecided is the nature of elastin itself, and how closely it is related to fibrous collagen (see previous discussion of Burton's work).

The use of trypsin may even be harmful in the preparation of fibrous collagen. Cassel and Kanagy (7) in 1949 made a study of the action of crude pancreatin on fibrous collagen and found that the amide nitrogen content of a collagen preparation appeared to be lowered if the preparation was treated with trypsin after a preliminary salt extraction. Further, although neither salt extraction nor trypsin treatment alone seriously altered the surface charge of the fibrous collagen as shown by electrophoresis, a combination of these two treatments produced a more acidic surface than was desirable in undegraded material. There was strong evidence that trypsin modified the fibrous collagen in such a manner that subsequent treatments resulted in degradation. Cassel and Kanagy suggested, therefore, that, since the main portion of the elastin is in the epidermis and would be removed in obtaining the corium split, trypsin should not be used. While they used a crude pancreatin in their studies, and their results may have been due, therefore, to other enzymes present as impurities, the use of crystalline trypsin presumably would not serve any purpose, as it would not attack the elastin.

Methods of extraction.—The ratio of hide to extracting solvent used in the preparation of fibrous collagen has varied from 1:3 to 1:10. While the larger volumes of solvent are certainly desirable from the point of view of complete extraction, it should be remembered that the increased efficiency of the extraction is not in direct proportion to the increase in volume of the

extracting solvent. If the experiment is to be carried out on a large scale, other practical considerations, such as the availability of equipment and the difficulties of evaporating the large quantities of water if the proteins in the aqueous solutions are to be studied, must be taken into account.

Another factor which must be considered is whether to use a still soak, stirring, or shaking. Kritzinger (21) made a study of the effect of agitation on the extraction of nitrogen-containing material from hide cubes by sodium chloride solution. He found that mild agitation increased the rate of extraction by about 10%; with severe agitation there appeared to be a much greater increase, but he interpreted this increase as due chiefly to severe mechanical action on the cubes. Again the ultimate choice will also probably depend on the size of the experiment and the equipment available.

Solutions for extraction

Water.—Water has not been extensively used as an extracting solvent. Lollar and Kiley (23), using two 1-hour extractions of cubed corium with water, found that 0.6% of the corium nitrogen was extracted. However, a large percentage of this nitrogen was probably from nonprotein nitrogenous compounds. Analysis for carbohydrate in the extract indicated that a small amount of mucoids or glycoproteins might have been extracted in addition to albumin.

Sodium chloride solution.—While extraction with sodium chloride solution will remove albumin and globulins, there is also evidence that some collagenous protein (i.e., hydroxyproline-containing protein) may also be extracted. Part of this collagenous material may be a true undegraded salt-soluble collagen (16). It is extracted in larger amounts from young than from mature skin (8).

Some of this hydroxyproline-containing protein may also be degraded fibrous collagen. DeBeukelaer and Marbach (11) showed that if a hide was shredded in a hammer mill with dry ice, 2.3% of the whole wet hide was collagen which was extracted by sodium chloride solution. However, if the collagen of the hide was protected from heat degradation by placing the hide in liquid nitrogen (−196°C.) and then grinding in a Wiley mill with dry ice, only 0.03% of the whole wet hide was salt-extractable collagen.

Kritzinger (20, 21) made an extensive study of the extraction of nitrogen-containing material from hides with sodium chloride solutions of various concentrations. He found that the 10% solution was the most efficient, although the 5% solution was only slightly less so. In experiments with ground hide, DeBeukelaer and Marbach (11) reported that after two 24-hr. extractions in a shaker with 10% sodium chloride solution at 8°C., the protein nitrogen extracted was 2.8% of the total hide nitrogen.

Using cubed corium split, Lollar and Kiley (23) found that 1% of the total corium nitrogen was extracted with two 1-hour extractions (with shaking)

and one 24-hr. soak with 10% sodium chloride. In Schmitt, Gross and Highberger's recently published method (33) for the purification of fibrous collagen, the corium was extracted 11 times with 10% sodium chloride solution (until no further protein was removed); these 11 extractions removed a total of 1% of the protein of the corium.

While a 10% sodium chloride solution has some bacteriostatic action, some bacterial (or autolytic) attack on the hide takes place if the extraction is prolonged. For example, Kritzinger (21) noticed that after a 72-hr. extraction with sodium chloride solution the hair was loose, even though the solution contained Merthiolate; after 84 hr. the attack on the collagen was noticeable, as evidenced by a sudden increase in non-coagulable protein in the extract. Cassel and Kanagy (7) also noted that after a hide had been kept 1 month in 5% sodium chloride solution at 6°C. with daily changes of the solution, the epidermal area was loose.

Alkaline phosphate buffer.—Alkaline phosphate buffer (pH 8 to 9) extracts the "alkaline buffer-soluble collagen" from skin (see discussion of soluble collagens in a previous section). In addition, it also removes at least some of the mucoids and glycoproteins (19, 31).

Neuberger (27) reported that approximately 4% of the total collagen of rabbit skin was soluble in neutral or slightly alkaline buffer.

Bowes, Elliott, and Moss (4) showed that corium which had been sectioned on a freezing microtome lost 8.5% of the total nitrogen by extraction with 0.1*M* phosphate solution until the nitrogen content of the extracts was very small. Since the corium had undergone no previous extractions, however, albumin and globulins, as well as alkaline buffer-soluble collagen and some mucoids and glycoprotein, are included in this figure. With bovine corium from an old animal, after previous exhaustive salt extractions, Schmitt, Gross, and Highberger (33) found that 9 extractions with 0.15*M* disodium phosphate removed only 0.2% of the total dry protein of the corium.

Citrate buffer.—Citrate buffer at approximately pH 3.5 is used to dissolve the "procollagen" or citrate-soluble collagen. Veis and Cohen (34) report that 2% acetic acid (pH 3 to 4) can be used in place of the citrate buffer. The amount of soluble collagenous protein thus obtained varies widely with the procedure used and also with the type of skin. Orekhovitch (30) reported that calfskin contains approximately 0.8% of "procollagen". On the other hand, Bowes, Elliott, and Moss (4) found, after extraction with phosphate, that 5% of the total protein of ground whole calfskin could be extracted with citrate buffer; with sectioned corium this figure was increased to 20% (see previous discussion of soluble collagens).

With young guinea pig skins Orekhovitch (29) reported that up to 10% of the collagen could be extracted. With minced rabbit skin which had been previously extracted with alkaline phosphate Harkness *et al.* (15) found that

6% of the total skin nitrogen could be extracted with citrate (pH 3.8). Using young rat skin Mikhailov (26) could extract 20% of the collagen with citrate buffer.

Half-saturated calcium hydroxide solution.—Extraction of hide with half-saturated calcium hydroxide removes mucoids and glycoproteins.

If the extraction is prolonged, some of the fibrous collagen may go into solution. Schmitt, Gross, and Highberger (33), after removing 1.2% of the total protein of bovine corium by extraction with salt and phosphate solutions, extracted the corium with half-saturated calcium hydroxide until the ratio of the hydroxyproline to glycine was the same in the extract as in the residue. Seventeen per cent of the corium protein was dissolved by the lime; this amount represents not only the mucoids and glycoproteins but fibrous collagen as well.

Lollar and Kiley (23) found that 0.7% of the corium nitrogen was removed by 2 extractions with half-saturated calcium hydroxide solution for a total of 26 hr. (one 3-hr. extraction with shaking and one 23-hr. soak), from corium cubes which had been previously extracted with water and sodium chloride solution. The soluble protein in this case was probably predominantly mucoid, as evidenced by the high carbohydrate content of the extract. Only negligible amounts of hydroxyproline were obtained in the extracts, which indicates that fibrous collagen was not dissolving under these conditions.

The question of the possible degradation of collagen by treatment with half-saturated calcium hydroxide solution must also be considered. Cooper and Sykes (9) have shown that decomposition of the amide groups of the side chains of collagen occurs if the hide is extracted for 72 hr. with half-saturated lime solution. Cassel and Kanagy (7) believe it is possible that some combination between the carboxyl groups of collagen and calcium occurs during lime extraction; this idea is based on the determination of the isoelectric point, which is raised from 5.8 to 7.7 during the process. They postulate that while this may be due to the removal of acid mucoid in the extraction, it might also be due to inactivation of the carboxyl groups by some type of combination with calcium.

Organic solvents.—Fibrous collagen preparations are usually treated with organic solvents in the course of their purification for two purposes: degreasing and dehydration. Degreasing solvents which have been used in the preparation of purified fibrous collagens are ether (3, 34), petroleum ether (5), and acetone with alcohol (7). Dehydration has been carried out with acetone (5), with alcohol followed by ether (7), or, in one method, by lyophilizing over a dessicant (34).

It is known that acetone causes denaturation of some globular proteins at the isoelectric point at room temperature, but denaturation does not occur at low temperatures (28). On the other hand, Gustavson (14) has shown that

bovine fibrous collagen which had been acetone-dehydrated, dried, and rehydrated, had the same properties as the native collagen. Since globular proteins, but not fibrous collagen, appear to be denatured by acetone at room temperature, it would seem a better procedure to use acetone only after the extractions with aqueous solutions had been completed.

Methods of determining purity.—There are no standard methods for assessing the purity of a fibrous collagen preparation. A number of criteria have, however, been developed by individual investigators.

Veis and Cohen (34) adapted a tool previously used for globular proteins for the characterization of native fibrous collagen. This involves a dye-protein precipitation method for the estimation of polar functional groups of the protein; it differentiates between native and mildly degraded collagens.

Loofbourow, Gould, and Sizer (24), who studied collagen from tendon, used a determination of the ultraviolet spectrum of a hydrolyzate of a collagen preparation as a tool in determining purity. Aromatic amino acids absorb at 280 mμ. Loofbourow *et al.* found that the ratio of the minimum absorption at 260 mμ to the maximum at 280 mμ increased as the collagen was purified, since the aromatic amino acid content was decreasing.

Schmitt, Gross, and Highberger (16), however, found that even their most highly purified collagen contained 0.41% of tyrosine on a dry, ash-free basis. This amino acid, since it has an aromatic nucleus, absorbs at 280 mμ. They are uncertain whether the tyrosine is present in an impurity which had not been removed by their exhaustive series of extractions (82 in all) or is actually present in chemical combination in the fibrous collagen. At the moment, then, all that can be said with certainty about the ultraviolet spectrum of a collagen hydrolyzate is that a preparation with high adsorption in the 280 mμ region is contaminated with other non-collagenous proteins.

In 1949 Cassel and Kanagy (7) set up certain minimum standards that a fibrous collagen preparation should meet, although they state that considerable tolerance in the specifications is intended. The ash should be less than 0.1%; the pH of the water extract should be between 6.0 and 7.0; the isoelectric point as determined by electrophoresis should be between 6.0 and 7.5 (higher than pH 7.5 indicates combined metals, lower than pH 6.0 indicates degradation); the total nitrogen should be between 17.8 and 18.1%; the amide nitrogen (as determined by heating for 20 hr. with 0.1 *N* hydrochloric acid at 90°C.) should be not less than 3.8%. A higher value (18.42%) for total nitrogen in an apparently highly purified fibrous collagen has been reported by Veis and Cohen (34).

The determination of the hydroxyproline content of a fibrous collagen preparation would probably be an excellent criterion of purity, since hydroxyproline is an amino acid which is essentially unique in collagen. However, probably owing in part to the difficulties encountered in the precise deter-

mination of hydroxyproline, it has never taken on this significance. Highberger (16) believes a figure of 14% hydroxyproline is probably near the actual value for bovine fibrous collagen.

Cassel and Kanagy (7) report that the total nitrogen of a fibrous collagen preparation is no index of purity, for even when the amide nitrogen of a preparation is very low, the total nitrogen may be as high as in undegraded collagen.

Other methods which have been used to define the purity of fibrous collagen preparations are acid-base titration curves (34) and electron microscope examinations (34, 35).

CONCLUSION

The preparation of pure fibrous collagen from skin is inherently very difficult and the goal has probably not been achieved up to the present time. In seeking to prepare a purified fibrous collagen the investigator should keep in mind the use for which it is intended and tailor the purification process to fit this purpose. For example, if it is essential that the fibrous collagen be undegraded, then any process that might possibly cause denaturation or degradation must be avoided, even at the expense of ultimate purification; on the other hand, if it is not essential that the fibrous collagen be completely in the native or undegraded form, more drastic methods of purification may be used.

In any case, with the methods available at the present time it is necessary to steer a middle course and to assemble a process of purification, realizing the drawbacks and limitations as well as the advantages of each step in the method.

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There is a hierarchy of facts. Some are without any positive bearing, and teach us nothing but themselves. There are, on the other hand, facts that give a large return, each of which teaches us a new law.—H. Poincaré, *Science and Method* (Dover, Del.: Dover Publications, 1952).

One of the clearest lessons to emerge from the history of science is that various scientific disciplines—seemingly unrelated—have a way of stimulating and fructifying each other in an unexpected manner. This complex back-and-forth interplay is the life and soul of science and technology—there can never be too much of it. The most impractical thing that can be done in designing and directing programs of scientific research is to worry overmuch about how "practical" they are. The secrets and treasures of Nature are hidden in the most obscure and unexpected places.

—*Strengthening American Science*, A Report of the President's Science Advisory Committee, Dr. J. R. Killian, Jr., *Chairman*. Dec., 1958.

THE MODE OF COORDINATION OF AMINO ACIDS WITH CATIONIC CHROMIUM IN ACID AQUEOUS SOLUTIONS

I. SPECTROPHOTOMETRIC STUDIES

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ABSTRACT

Spectrophotometric curves on chromium complexes formed with α-, β-, γ-, and ε-amino acids at 1, 2, and 3 moles/mole chromium and aged to equilibrium at pH 2.50, 3.16, and 3.82, show that the molar extinction coefficients increase from the α to the ε forms, which is opposite to the effect which could be anticipated from chelation of both carboxyl and amino groups. The extent of coordination, as revealed by the spectrophotometric curves, appears to be approximately proportional to the pK values of the carboxyl groups, which are influenced by the number of carbon atoms separating the carboxyl and amino groups. A similar pattern is revealed by studying the fixation of chromium by pelt from solutions masked with α-, β-, and γ-amino-n-butyric acids, the masking power increasing from α to γ. These results also appear to confirm the suggestion of one of the authors (1) that the stability of coordination of an acidic group to chromium is inversely related to the dissociation constant of the acid.

INTRODUCTION

Research into the mode of combination of various organic acids and bases with chromium salts has been carried out for many years in these laboratories, and much of the work was summarized by Shuttleworth some years ago when it was discussed in a paper dealing with the theory of chrome tanning (2). A recent publication by Ramaswamy and Nayudamma (3) in this *Journal* included some results on a spectrophotometric investigation of chromium/glycine complexes and led the authors to undertake a more general investigation of the complexes formed between chromium and a series of amino acids in which the acid and basic groups are separated by an inert

hydrocarbon chain. Visual observations of the color changes in a solution of chrome alum produced by masking with amino acids showed that marked alterations took place. As the amount of amino acid increased with respect to chrome there was a tendency for the color of the solution to become almost violet in the case of the α-amino acids, while with β-, γ-, and ε-amino acids a pronounced yellowing took place giving rise to emerald-green solutions; this latter trend was progressive as the distance between the amino and carboxyl groups increased. All the changes in coloration were more pronounced at pH 3.8 than pH 2.5. The blue-violet color formed by the α-amino acids is however anomolous, and it was decided to examine solutions of chromium/amino acid complexes in the spectrophotometer. This work forms the subject of the present report.

Theis and coworkers (4) who pioneered the investigation of chromium complexes using the spectrophotometer do not appear to have taken into account the fact that the addition of organic acids alters the pH of a solution of chromium salts, and hence the changes which they recorded may in part be due to this factor. Shuttleworth (2) overcame this difficulty some years ago by comparing solutions in which the oxalate ion was added in the form of a salt rather than from the free acid, and at the same time he adjusted his solutions to predetermined pH levels with acids whose anion had negligible coordination potential. This technique has been followed in the present work.

EXPERIMENTAL

A stock solution of 0.5*M* reagent-grade chrome alum was prepared. Aliquots of this solution were taken, and solutions of the various amino acids were added in such quantity that the molar ratios of amino acid/chromium were 1, 2, and 3. Three separate aliquots were prepared at each molar ratio for all the amino acids studied and were adjusted by the addition of *N* hydrochloric acid or *N* potassium hydroxide so that the equilibrium pH lay at one of three predetermined values, namely 2.50, 3.16, or 3.82. Equilibrium was attained by alternately adding acid (or alkali), warming on a hot plate at about 60°C. for 2 hr., cooling, and readjusting the pH until no further adjustment was required after two successive heatings. Each masked chrome liquor so prepared was then made up to volume so that the final solution was 0.33*M* with respect to chromium. It was found that the amount of added water was in the order of only 5% of the total volume and that it made a negligible alteration to the pH of the solution. After preparation the solutions of chromium sulfate/amino acid complexes were aged at room temperature for at least one month prior to examination in the spectrophotometer. The stock solutions were all 0.33*M* with respect to chromium, and these were diluted 25 times immediately prior to examination in a Beckman model DU spectrophotometer at 20°C. The solutions as used in the spectropho-

tometer contained 0.1% Cr_2O_3. Each curve took about 10 minutes to complete. Measurements were commenced at a wavelength of 320 mμ and continued to 620mμ. After completion of each curve the optical density at 320 mμ was checked, and in most cases some change was observed. As this change was only in the order of .005 it has been treated as insignificant for the purposes of the present paper.

RESULTS

The form of the curves is very similar in general outline to those reported in previous work (2, 3, 4) and shows pronounced maxima in two regions,

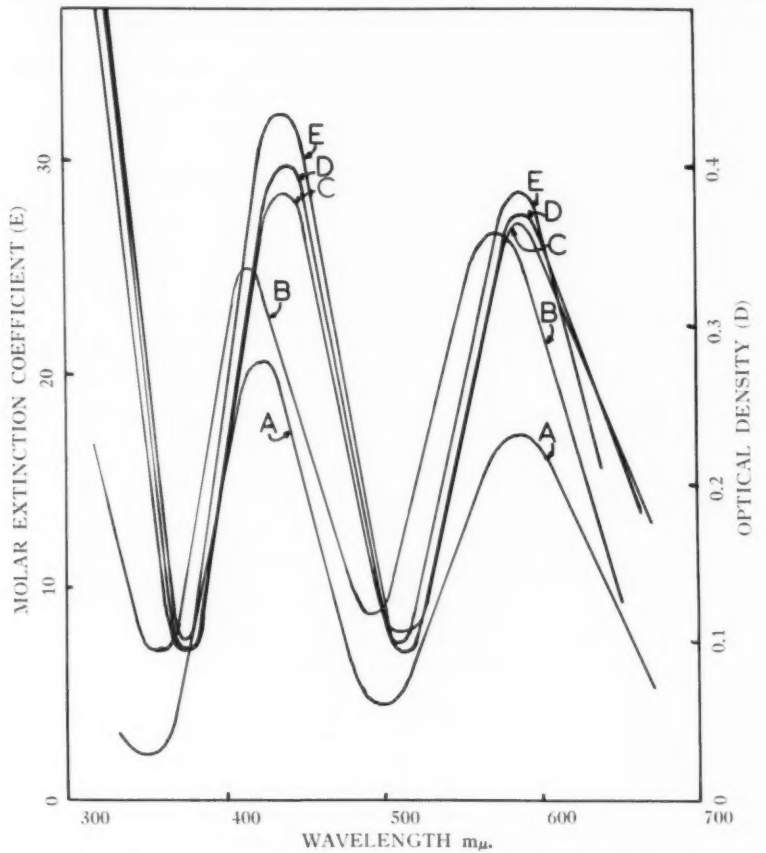

FIGURE 1.—Spectrophotometric absorption curves of solutions of chrome alum masked with 2 moles amino acid/mole Cr after adjustment to pH 3.16 and aging. A = no amino acid, B = glycine, C = β-amino-n-butyric acid, D = γ-amino-n-butyric acid, E = ε-amino-n-caproic acid.

roughly around 420 and 570–80 mμ. These will be termed, respectively, the blue and yellow peaks in this report. Compared with the curves obtained for unmasked chromium sulfate at the same pH value there is a marked increase in absorption when amino acids are present, thus indicating that amino acid has complexed with the chromium. This is shown diagramatically in Fig. 1 for 2 moles of amino acid/mole chromium after adjustment to an equilibrium pH of 3.16 and subsequent aging for one month prior to determining the absorption characteristics. Data for solutions containing 1 and 3 moles of amino acid/mole chromium equilibrated at other pH's are given

TABLE I

WAVELENGTH OF ABSORPTION MAXIMA FOR CHROMIUM SULFATE MASKED WITH VARIOUS AMINO ACIDS

Amino Acid	Moles Amino Acid/ Mole Chromium	Blue Peak			Yellow Peak		
		Eqm.pH of Solution Prior to Dilution					
		2.50	3.16	3.82	2.50	3.16	3.82
Nil	–	419	423	–	584	583	–
α-amino acetic (glycine)	1	418	418	420	577	576	574
α-amino-n-butyric	1	420	420	421	577	576	574
β-alanine	1	421	422	422	580	578	577
β-amino-n-butyric	1	422	422	422	581	580	577
γ-amino-n-butyric	1	421	422	421	579	579	576
ε-amino-n-caproic	1	420	423	424	578	576	575
α-amino acetic (glycine)	2	422	418	415	578	574	569
α-amino-n-butyric	2	421	426	–	580	578	–
β-alanine	2	422	431	440	581	584	580
β-amino-n-butyric	2	436	436	437	586	586	585
γ-amino-n-butyric	2	435	438	438	584	584	584
ε-amino-n-caproic	2	430	437	439	581	582	583
α-amino acetic (glycine)	3	422	418	414	573	567	564
α-amino-n-butyric	3	–	426	–	–	578	–
β-alanine	3	442	441	441	586	586	585
β-amino-n-butyric	3	441	441	442	586	586	586
γ-amino-n-butyric	3	440	440	440	586	584	582
ε-amino-n-caproic	3	438	434	440	586	586	576

in Table I for the wavelength at maximum absorption and in Table II for the molar extinction coefficients calculated according to the method given by Weisburger (5).

TABLE II

MOLAR EXTINCTION COEFFICIENTS* OF CHROMIUM SULFATE MASKED WITH VARIOUS AMINO ACIDS

Amino Acid	Moles Amino Acid/ Mole Chromium	Blue Peak			Yellow Peak		
		Eqm.pH of Solution Prior to Dilution					
		2.50	3.16	3.82	2.50	3.16	3.82
Nil	–	16.2	21.0	—	14.8	17.6	—
α-amino acetic (glycine)	1	19.7	22.1	25.1	22.1	24.3	25.0
α-amino-n-butyric	1	20.1	22.4	26.7	22.2	25.5	26.2
β-alanine	1	20.6	21.1	21.9	24.6	26.3	28.1
β-amino-n-butyric	1	21.0	22.0	22.9	24.6	26.4	29.1
γ-amino-n-butyric	1	20.1	20.8	22.2	24.1	25.8	28.9
ε-amino-n-caproic	1	20.0	22.1	23.8	24.4	26.4	28.1
α-amino acetic (glycine)	2	22.9	24.9	25.0	25.8	27.0	27.8
α-amino-n-butyric	2	21.8	26.5	—	24.0	27.4	—
β-alanine	2	24.4	27.6	31.9	25.1	27.5	30.8
β-amino-n-butyric	2	25.3	29.0	28.1	25.7	27.5	29.6
γ-amino-n-butyric	2	27.0	30.2	30.1	27.0	27.6	30.8
ε-amino-n-caproic	2	25.8	32.8	34.6	26.7	29.2	31.7
α-amino acetic (glycine)	3	24.4	24.5	24.3	26.6	27.8	28.7
α-amino-n-butyric	3	—	26.1	—	—	27.0	—
β-alanine	3	29.5	32.6	32.1	26.6	28.0	30.0
β-amino-n-butyric	3	30.0	33.4	33.7	27.0	28.7	29.6
γ-amino-n-butyric	3	31.9	35.4	35.3	27.8	30.0	31.5
ε-amino-n-caproic	3	32.2	36.0	37.1	29.1	31.5	32.5

*Molar Extinction Coefficient $E = \frac{D}{cd}$ (5) where

c = concentration of chromium in moles/1.
d = light path in cm.
D = optical density.

In all this work c was maintained at 0.0133 moles/1. and d was 1 cm.

INTERPRETATION OF RESULTS

Figure 1 shows the progressive increase in molar extinction coefficient (E) as the number of carbon atoms between the amino and carboxyl groups increases from one to five. The increase of optical density for the amino acid complexes is much more pronounced relative to the unmasked chrome alum in the yellow region than in the blue region at about 420 mμ, although the differences between individual amino acids are greater in the blue region. The magnitude of shifts in the wavelength of maximum absorption can be seen from Fig. 1 and from the data in Table I. The changes which do occur

become much more pronounced as the molar ratio of amino acid to chromium increases from one to three. Changes are also more pronounced at pH 3.82 than at 2.50. At the blue peak there is a progressive increase in the wavelength of maximum optical density as the distance between the charged groups of the amino acids increases, i.e., α-amino acids have absorption maxima at the shorter wavelength and the ε-amino acid has a maximum at the longer wavelength. With the exception of the α-amino acids the wavelength for maximum absorption tends to be longer for masked complexes than for unmasked chrome sulfate. A somewhat similar but less pronounced trend is also noted for the yellow peaks in the 580 mμ region.

In attempting to find some formal sequence for the results of this investigation cognizance must be taken of two factors. First, Theis (4) has sug-

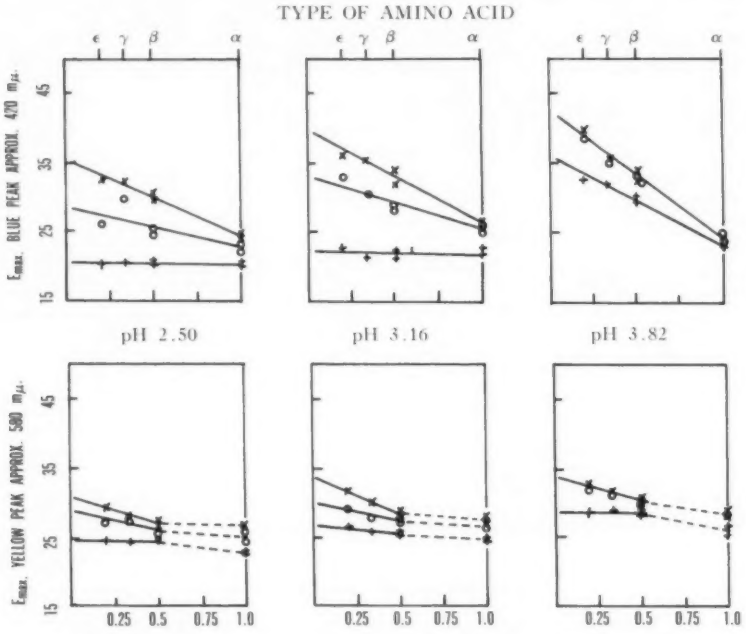

FIGURE 2.—Plots of Molar Extinction Coefficient (E max) of chromium/amino acid complexes against reciprocal of number of carbon atoms separating polar groups in the amino acids. In all graphs

+ . . . + represents 1 mole amino acid/mole Cr
○ . . . ○ represents 2 moles amino acid/mole Cr
× . . . × represents 3 moles amino acid/mole Cr

gested that the penetration of a complexing molecule or radical into the coordination sphere of a chromium atom would tend to insulate the outer electron shells of the chromium and increase the absorption maxima; hence the present results would indicate that coordination has in fact occurred. Second, Cohn and Edsall (6, 7) have pointed out an approximately linear relationship which exists between various ionization constants of amino acids in solution (e.g., pH values, pI values, etc.) and the reciprocal of the distance between the polar groups; for convenience this latter function is expressed as the number of carbon atoms separating the amino and carboxyl groups.

In view of the trends which can be observed by inspecting Tables I and II it was decided to plot the results for increase in absorption maxima (molar extinction coefficient) as a function of the reciprocal distance between the polar groups of the amino acids. For ease of comparison six graphs relating to the two peaks at 3 pH levels are all included in Fig. 2. In all the graphs the horizontal axis is the reciprocal of the number of carbon atoms between the polar groups in the amino acids; for ease of reference the points corresponding to the α, β, γ, and ϵ positions are marked. The vertical axes are the molar extinction coefficients at the two peaks. With the exception of the peaks produced by the α-amino acids in the yellow region all the graphs show a number of similarities: (*a*) At any given molar ratio there is an increase in the absorption maxima with increasing pH. (*b*) With two exceptions there is a steady increase in absorption maxima as the distance between the polar groups increases. These are in the blue region for the one molar level at the lower pH's, and the anomolous position which the α-amino acids have in their absorption in the yellow region. (*c*) At the highest pH level (3.82) the absorption maxima for 2 and 3 moles of amino acid per mole chromium coincide, and the distance between polar groups is seen to have an effect at the 1 molar level. (*d*) The spread between the maxima at 1 and 3 moles is much greater in the blue region than the yellow.

If we accept Theis's concept that an increase in absorption maxima is brought about by the penetration of complexing ions, then it would appear that the ϵ-amino acids are better complexing agents than the α-amino acids. This finding is demonstrated graphically for the masking of chromium sulfate with 2 moles amino acid/mole chromium at pH 3.16 in Fig. 3: the form of the curves is similar for the other molar and pH levels.

Figure 3 shows the wavelength of maximum absorption at the two peaks and the corresponding molar extinction coefficients plotted against a common horizontal axis recording the dissociation constant of the carboxyl group. For ease of interpretation the acids studied in this work are indicated on the graph at their appropriate pK's. All these properties show to a first approximation a linear relationship and indicate that complex formation at a particular pH and molar ratio is primarily dependent on the dissociation constant of the amino acid. Attention must, however, be drawn to the somewhat

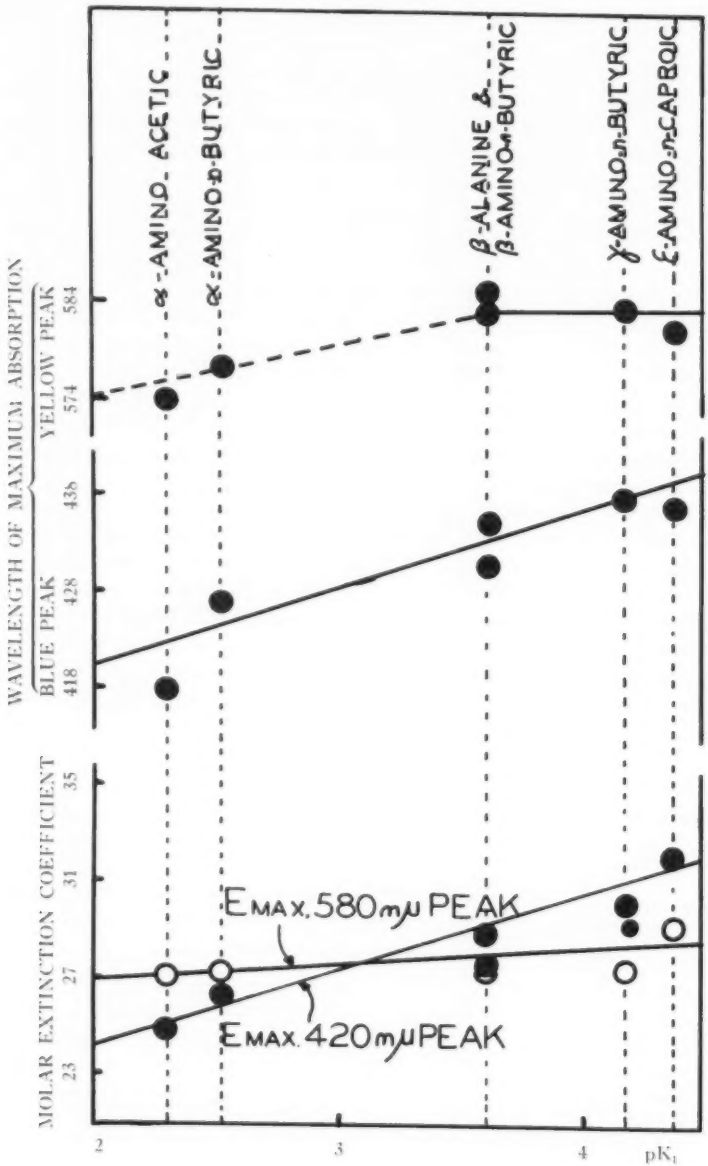

FIGURE 3.—Plots of various properties of the complexes formed by masking chromium sulfate with 2 moles amino acid/mole Cr and adjusting to an equilibrium pH of 3.16 as a function of the pK_1 value of the amino acid substituent.

anomalous effect which the α-amino acids have on the yellow absorption maxima. Here it will be seen that the β-, γ-, and ε-acids exhibit a maximum absorption at almost identical wavelengths, but that the maximum absorption of the α-amino acids is at a lower wavelength. It is almost certain that this lower maximum is a major cause contributing to the blue-violet color which is exhibited by these α-amino acid complexes. The constant wavelength of maximum yellow absorption, coupled with the steady increase in the wavelength of maximum absorption in the blue region with greater distance between polar groups, is adequate explanation for the color changes which are observed visually.

The effect of the α-amino acids is particularly important, as glycine, which constitutes almost 1/3 of the amino acids in collagen, has on occasion been used as a model substance for formulating mechanisms of chrome tanning (3, 4, 8). It has been assumed that the α-amino group has formed a chelate ring with the chromium and the adjacent carboxyl group. The present work would indicate that this inference is incorrect and that apart from the light absorption at one group of maxima the behavior of glycine and α-amino-n-butyric acid follows a progressive trend with β-, γ-, and ε-amino acids which are unable to form chelate rings with chromium involving both amino and carboxyl groups. Gatehouse (9) has pointed out the difficulties encountered in associating the colors produced by complex chromium salts with specific bonds, and until further evidence is available, the present authors would suggest that the blue-violet cast of the α-amino acid chrome complexes is due to an electrostatic disturbance of the unstable outer electron shell of the chromium atom by the positively charged amino group, an effect which would fall off rapidly as the distance between the amino group and the chromium atom increases.

CONCLUSIONS

The work reported in this paper has used amino acids as model substances for elucidating the mechanism of chrome tannage. Spectrophotometric investigations have demonstrated that under comparable conditions of pH and molar ratio more complexing takes place with those amino acids whose amino group is well separated from the carboxyl group by a hydrocarbon chain. Thus, ε-amino acids are better complex formers than α-amino acids. No indication of chelate ring formation involving amino groups has been found, nor was it expected in the light of previous work on the reaction between acidic solutions of chromium sulfate and amine bases (2, 10). Furthermore, the finding that the reaction between chromium sulfate and amino acids bears a direct relation to the dissociation constant of the carboxyl group is in agreement with Bjerrum's work on thiocyanate complexes (11).

In relating these results to recent work on the mechanism of chrome tanning (2, 12, 13, 14, 15) no contradictions are found. Under the aqueous acid conditions employed in this investigation reaction can take place between

the carboxyl group of an amino acid and chromium sulfate which does not involve the amino group. Indeed the presence of an amino group immediately adjacent to the carboxyl group would seem to be the principal factor in retarding coordination of the latter to chromium. It would be expected that if the γ- and ε-amino acids formed more stable complexes than the α-amino acids, then these complexes would be less efficient as tanning agents. Some preliminary studies by one of us (16) have in fact shown this to be the case, as is indicated by the results in Table III. These results demonstrate that

TABLE III

FIXATION OF CHROMIUM BY PELT FROM SOLUTIONS MASKED WITH 2 MOLES AMINO ACID/MOLE CHROMIUM AT pH 3.16

Masking Agent	Fixation of Chromium	
Nil	0.74	m. moles Cr/g collagen
α-amino-n-butyric acid	0.35	"
β- " "	0.23	"
γ- " "	0.17	"

for the three isomeric amino-n-butyric acids the progressive increase in their reaction with chromium sulfate produces complexes which are more resistant to penetration by the carboxyl residues in collagen. In this particular instance steric hindrance effects are equal, and the only variable is the number of carbon atoms separating the polar groups. Hence, it would appear that these few tanning trials provide additional support for the concepts put forward earlier in the paper.

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LIFE LINES

Brief Biographies of Our Contributors

Dr. Clara Deasy holds the Ernest Griess Fellowship and is Associate Professor of Basic Science in Tanning Research at the University of Cincinnati where she completed both her undergraduate and postgraduate work. She has taught at Oberlin College and Temple University Medical School and carried out research on proteins at the University of Illinois and at California Institute of Technology. She has some thirty scientific publications to her credit.

Dr. S. G. Shuttleworth graduated from Rhodes University in 1930. He obtained his Master's and Doctor's degrees from the same University in 1935 and 1937. He was the first Proctor Memorial Fellow at the University of Leeds in 1939 and later held the Hunt Rankin Fellowship at Lehigh. After a short period as Technical Director of Bona Allen Co., Georgia, he returned to South Africa in 1941 to assume directorship of the newly established Leather Industries Research Institute, a position which he still holds. Dr. Shuttleworth's principal interest has been in the field of chrome chemistry, and he has published over 200 scientific papers and reports on various aspects of the hide and skin, leather and footwear industries. He is a Fellow of the Royal Institute of Chemistry and of the British and South African Boot & Shoe Institutes.

Dr. R. L. Sykes graduated with First Class Honors from Leeds University in 1950, and took his Ph.D. from the same institution in 1952. He was awarded the LeBlanc Medal by the Faculty of Technology of Leeds (1950), held the Proctor Memorial Fellowship (1950-51), and received the Donald Burton Prize of the Society of Leather Trades' Chemists in 1953. After 18 months in the British Colonial Service in East Africa, where he worked in an advisory capacity to the hides, skins and leather industries, he joined the Leather Industries Research Institute, Grahamstown, South Africa, as Senior Research Officer in 1954. His brief professional career has already resulted in a score of publications in various technical and scientific journals.

U. S. science . . . has a scope and depth unequaled anywhere in the world. In less than a generation the U. S. has wrested scientific leadership from its birthplace, Europe, and since 1945 over half of all Nobel prizes in the sciences have been awarded to Americans.

—*Strengthening American Science*, A Report of the President's Science Advisory Committee, Dr. J. R. Killian, Jr., *Chairman*. Dec., 1958.

ALCA NEWS

Proceedings, Reports, Notices, and News

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TENTATIVE PROGRAM—1959 ALCA CONVENTION

GRAND HOTEL, MACKINAC ISLAND

SUNDAY, JUNE 14—WEDNESDAY, JUNE 17

PRESIDENT'S ACTIVITIES

Sunday, June 14, 6 P.M.—Reception
Monday, June 15 —President's Address
Tuesday, June 16 —Banquet. Guest Speaker: Dr. Charles Noble, Syracuse University

TECHNICAL PAPERS

(*To be presented Monday morning and Tuesday morning and afternoon.*)

Dynamic Electrical Behavior of Untanned Hide Containing Sorbed Water. Lee P. Witnauer.—The dynamic electrical properties of untanned hide substance were investigated. The effect of varying the moisture content of the hide from 0 to 29% on the observed dielectric constant and loss factor was studied over the temperature range −20° to 100°C. and the frequency range 50 to 100,000 c.p.s. The observed dielectric constant of the hide-water systems varied directly with temperature and inversely with frequency. This is exactly the same type of response exhibited by many polymeric systems. The results indicate that water exhibits a typical plasticizing action on hide substance.

Tanning with Glutaraldehyde. M. L. Fein, E. H. Harris, Jr., J. Naghski, and E. M. Filachione.—In this study full sheepskins (Syrian) were tanned with glutaraldehyde under various conditions to evaluate the tanning properties of this aldehyde and its comparison to other aldehydes. Measuring the disappearance of glutaraldehyde from the tanning liquor provided a sound basis for evaluation of the over-all rate of tanning and fixation. Tanning was effected over a wide range of conditions. The rate of tanning and uptake of glutaraldehyde increased rapidly with increase of pH and concentration. Maximum shrink temperature also was attained rapidly, and in the higher pH ranges it was reached in about one hour. Under certain conditions complete exhaustion of glutaraldehyde could be obtained from the tanning liquors. This behavior is in marked contrast to that observed in the case of formaldehyde or glyoxal. Under comparable conditions of tanning with these three aldehydes the rate of tanning increased in the order: glyoxal, formaldehyde, and glutaraldehyde. The skins tanned with glutaraldehyde under the various conditions were processed with regular packs into garment leather in a commercial tannery. Leather judged to be satisfactory was obtained under a wide variety of tanning conditions. Tested against a synthetic perspirant this leather showed unusual resistance to deterioration in contrast to formaldehyde and glyoxal leather. The glutaraldehyde tannage was also compatible in combination with conventional tannages such as chrome, vegetable, and alum.

Studies Concerning the Origin of Salt Stippen and Its Chemical Nature. Jean Tancous and Fred O'Flaherty.—For many years tanners have been annoyed with a grain defect known as salt stippen. Histological studies have revealed that stippen causes rupturing of the internal tissues of the hide, that it develops during the curing process, and that bacteria are secondarily involved. Spectrographic and chemical analyses have revealed interesting information concerning the chemical nature of the salt stippen crystals. Data and slides will be presented. Possible preventive measures will be discussed.

4-Nitrophenyl Esters and Carbonates as Leather Fungicides. Sverre Dahl and A. M. Kaplan.—4-Nitrophenyl derivatives lacking a free phenolic OH group have generally been neglected for serious consideration as leather fungicides in spite of the well-known employment of the parent compound for this purpose. It has been assumed that among such derivatives a free OH group is essential for high fungitoxic potency. However, it has recently been shown that bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate in leather hydrolyze under mildew-growing conditions with liberation of the free nitrophenols. The two bis carbonates thus are as effective leather mildew inhibitors as the phenols themselves. These

findings prompted an investigation of additional carbonates and esters of 4-nitrophenol and 2-chloro-4-nitrophenol. The results of this investigation are reported and discussed in the present paper. All these compounds behaved like the bis carbonates, i.e., they were all effective leather fungicides. Their potential advantages over 4-nitrophenol are discussed.

The Soaking of Salt-dry India Goatskins. T. C. Thorstensen and James Tirrell.—The problem of soaking salt-dry India goatskins has been studied by means of pilot-plant and full-pack experiments. The effects of temperature and various soak additives on leather quality will be reported.

Effects of Gamma Radiations on Leathers and Rawhide. V. G. Vely, N. D. Gallagher, and M. B. Naher.—A study was made to obtain statistically valid data on the effect of several levels of irradiation from a cobalt 60 gamma source on leathers and rawhide. To evaluate the effect of irradiation, shrinkage temperature, breaking strength, and elongation properties were compared of irradiated and non-irradiated control samples selected by a matched pair scheme. A high level of irradiation (1×10^8 reps) resulted in significant decreases in all the properties. Vegetable-tanned leather showed a greater decrease in shrink temperature but less decrease in breaking strength than chrome-tanned and retanned leathers. Pickled rawhide stock was adversely affected by 1×10^7 reps as indicated by significant decreases in shrinkage and breaking strength. The effect on rawhide of several organic compounds in the presence of gamma radiation was also investigated. Glutaraldehyde decreased the severity of detrimental changes. This was attributed to the slight tanning effect of this compound.

The Isolation of Elastic Tissue of Animal Skin. Conrad L. Ornes and William T. Roddy.—In recent years the behavior of the elastic tissue of animal skin has been under investigation to elucidate its properties. These investigations will be reviewed, and methods of isolation of the elastic tissue from skin and leather will be presented. The isolation methods developed can be used to determine the modification in the elastic tissue brought about by the various chemicals used in processing skin into leather.

Zirconium Tannage. VIII. The Stratigraphic Distribution of Zirconium in Leather. I. C. Somerville, J. Wendkos, L. V. Hetzel, and H. R. Franecke.—A brief report is given on progress in development of a process in which an insoluble zirconium salt is added directly to acid in the presence of hide. In the course of the experiments information was required on the distribution of zirconium and silicon through the skin. This led to stratigraphic analyses of leathers tanned with a series of commercially available zirconium compounds in comparison with chromium tannage. These results are presented and their significance discussed.

The Different Effects of the Sorption of Calcium and of Sodium Ions on the Swelling of Hide Collagen. E. D. Mellon, H. A. Gruber, and S. A. Viola.—The short-time sorption of calcium and sodium ions by purified collagen from the corium of cattlehides indicates that equilibrium occurs in a very short time for both the ion sorption and the swelling phenomena. Therefore, measurements of these phenomena can be made before secondary changes occur in the collagen. Quantitative measurements of the amount of calcium and sodium ions absorbed from solutions of the mixed ions permit comparison of the ions under competitive conditions. Calcium ions are much more strongly absorbed than sodium ions, and displace specifically bound sodium ions. The absorption of both calcium and sodium ions is completely reversible. In the presence of limited amounts of calcium ions most of the calcium is specifically bound. In the presence of sufficient calcium ions most of the sodium ions remain in the multilayer water of hydration, and the concentration of sodium ions in this absorbed water is closely related to the concentration in the surrounding solution. Increased salt concentration in the multilayer bound water increased the degree of swelling. Calcium ions appear to be bound by only one charge; therefore, the binding sites appear to be fairly well separated, and absorption of calcium ions can be expected to alter the electrical properties of the collagen.

Dyewoods in the Leather Industry. Howard B. Simmons.—A discussion of the historical background and economic position of dyewoods. The use and utility of dyewoods in the leather industry will be developed and their comparison to vegetable tannins indicated.

A Dialdehyde Starch Pretannage for Rapid Vegetable Tanning of Sole Leather. C. W. Beebe, M. L. Happich, J. Naghski, and W. Windus.—A process is described for the tannage of sole leather in one week, using a pretannage with dialdehyde starch. Tests indicate that a sufficient pretannage may be obtained with a solution of 5% dialdehyde starch (based on hide weight) and a pH of approximately 8. The pH of the hides going into this liquor may be varied within wide limits. Results are given for hides adjusted to pH 4.8 and 8.5. The time required for the pretannage in a still or rocker vat is no more than 48 hours. After the pretannage the hides are given a vegetable tannage in strong liquors of approximately 15% tannin with a pH of 4.0. This tannage requires 3 to 5 days in a still vat. The time required for either tannage may be shortened considerably by the use of mechanical motion, such as a drum or a paddle. The vegetable tanning liquors may be restrengthened and used repeatedly. Chemical and physical tests have been made on some of these leathers which had been extracted and finished at a commercial tannery. The results obtained have been similar to those obtained with usual commercially tanned leathers.

Rapid Moisture Measurement of Leather. R. Stubbings and L. Ambrose.—The principles of change in dielectric constant and resistivity have been proposed for the determination of moisture in various organic and fibrous materials including leather, wood, paper, etc. A study was made of the precision, reliability, reproducibility, and general utility of these methods as applied to commercial leather in various stages of processing. A portable direct-reading instrument for the rapid and nondestructive determination of moisture in leather from 11% to 40% is described, and some practical areas for production use in the tannery are suggested.

TANNING SYMPOSIUM

Retannage Of Chrome-tanned Leather. *Moderator*—Mr. Herbert Tetreault, A. C. Lawrence Leather Company, assisted by Mr. Elcanna Peterson, Geilich Leather Company

Zirconium Retannage—Dr. Ian Somerville, Rohm & Haas Company

Resin Retannage—Mr. Frank Edmonds, American Cyanamid Company

Vegetable Retannage—Mr. Melvin Herman, Armour Leather Company

Chrome Retannage—Mr. Herbert Tetreault, A. C. Lawrence Leather Company

TECHNICAL MEETINGS

The various technical committees will meet on Sunday afternoon and evening. Rooms and hours are to be arranged by F. Klimpl.

EXHIBITS

Various exhibits of products and equipment of interest to the tanning industry will be set up in the main lecture hall. These booths have been arranged by Oscar Wederbrand, Chairman of the Ways and Means Committee.

ENTERTAINMENT

Professional entertainment will be presented on Monday evening, followed by a dance. Dancing will also follow the banquet on Tuesday evening.

GOLF

The golf tournament has been scheduled for Monday afternoon, with a rain date Tuesday afternoon. The golf committee is composed of W. B. Hartnett, chairman, F. Chadwick, and M. Lindsay.

LADIES' ACTIVITIES

The ladies' committee has arranged a program including a putting contest, a tour of Fort Mackinac, luncheons, and card parties. Mrs. Arthur Carlson, Jr., chairman, will be assisted by Mrs. M. Maeser, Mrs. Howard Willis, Mrs. J. Earle Dahm, Mrs. Ernest H. Stein, Mrs. C. D. Wilson, Mrs. B. A. Grota, Mrs. A. G. Fleisch, Mrs. R. Nelson, Mrs. J. Thornton, Mrs. C. Retzsch, and Mrs. R. Stubbings.

CONVENTION COMMITTEE

Robert Stubbings, Chairman
Fred Klimpl, Vice-Chairman
Oscar Wederbrand—Ways and Means
Walter Wachholz—Transportation
Ben Grota—Publicity
W. B. Hartnett—Golf
Mrs. Arthur Carlson, Jr.—Ladies

ALCA-ASTM JOINT COMMITTEE ON LEATHER

Meeting November 13–14, 1958
Benjamin Franklin Hotel
Philadelphia, Pa.

The subcommittee and section meetings began at 10:00 A.M. on November 13 and continued to noon, November 14, 1958. A list of those in attendance follows: H. R. Miller, E. I. du Pont de Nemours & Co.; J. R. Kanagy, National Bureau of Standards; H. Haemisegger, Newark Leather Finish Co.; C. Paul McKee, International Shoe Co.; G. L. Somer, Armour Leather Co.; R. M. Lollar, Tanners' Council Laboratory, University of Cincinnati; N. C. Benrud, S. B. Foot Tanning Co.; R. Shaw, Rohm & Haas; G. Leithauser, General Motors Corp.; M. M. Baldwin, Battelle Memorial Institute; R. L. Young, Jr., International Shoe Co.; Charles Dudley, Dow Corning Co.; J. Naghski, Eastern Regional Research Laboratory; E. D. Compton, Eagle-Ottawa Leather Co.; C. K. Knisely, Thompson & Co.; M. H. Olson, Minnesota Mining & Machine Co.; James M. Cassel, National Bureau of Standards; A. N. Compton, E. F. Houghton and Co.; M. Maeser, United Shoe Machinery Corp.; R. G. Ashcraft, Endicott-Johnson Corp.; George Butz, Endicott-Johnson Corp.; J. Bassett, A. C. Lawrence Co.; C. W. Mann, Quartermaster Research and Development Center; A. E. Chouinard, Lowell Technological Institute; S. T. Tu, United Shoe Machinery Corp.; S. S. Kremen, Leather Research Corp.; E. M. Filachione, Eastern Regional Research Laboratory;

R. F. Wirt, Hercules Powder Co.; M. Bailey, U. S. Navy Research and Development Facility; B. F. Lewis, T. Olsen Testing Machine Co.; L. P. Witnauer, Eastern Regional Research Laboratory; S. S. Saryan, Allied Kid Co.; G. von Fuchs, Consultant; T. C. Thorstensen, Lowell Technological Institute Research Foundation.

The Joint Committee convened at 1:00 P.M., November 14. The first order of business was the presentation of reports of meetings of subcommittees and sections. These reports are appended.

Chairmen of subcommittees were urged to submit items for discussion to their members prior to meetings to allow sufficient time for study before the meeting.

In order to create more interest in future meetings of the committee, it was suggested that half a day might be scheduled for the discussion of a subject of general interest. The proposed subject for the next meeting is a discussion of the significance of tests.

C. W. MANN
Secretary

Subcommittee I. Nomenclature, Definitions and Applicability.—The committee, with a quorum of 4 out of 5 members, approved (with a suggestion for editorial revision in the actual wording) the significance and the precision statements included in two prospective methods:

1. Tentative Method for the Cold Crack Resistance of Upholstery Leather, as submitted by subcommittee III, Section 5.

2. Tentative Method for the Determination of the Thickness of Leather Specimens, as submitted by subcommittee III, Section 2.

The subcommittee is cooperating with other sections on other methods; no other methods are, however, before it for action at the present time. Subcommittee I would like to restate its understanding of the decisions made by the Joint Committee earlier which should guide the sections of the subcommittees:

1. Every method must include a portion on Significance, where this word is used in the sense described by ASTM "Proposed Recommendations on Form of ASTM Methods of Test, First Draft, January 1957".

2. Existing methods in the ALCA Methods Booklet shall have valid statistical estimates of precision before being presented as a proposed ASTM method. These estimates should include:

a. The standard deviation of replicated measurements made upon adjacent leather specimens, often described as the inherent test error.

b. The component of variance standard deviation of measurements from hide to hide in the approved sampling location.

3. The subcommittee will accept methods not now in the ALCA methods booklet without precision estimates if in its decision the technical section has

reached an impasse in its development work. When the suggested method has become tentative, it is desired that the use of the method furnish the desired precision estimates before the method is approved as a standard method.

ROBERT M. LOLLAR

Subcommittee II. Sampling and Conditioning for Physical Testing.—The first draft of the method for sampling cowhide leather for physical tests was reviewed and discussed in detail.

The committee agreed to limit the method to cattlehides, except sole leather, and to change the title accordingly. Further consideration will be given to the sampling in only one or several areas on each side. It was agreed that the location of test specimens within the sample area would be precisely defined for greater uniformity in testing.

Questions regarding the direction of the long dimension of each specimen with respect to the backbone direction were not resolved. The direction generally will be perpendicular except as otherwise specified. Exceptions will be enumerated either in the individual test methods or in the sampling procedure.

Basic data on the dimensions of small skins will be obtained by Joe Bassett for use in preparing a sampling method for this leather.

C. W. MANN

Subcommittee III.—*Section 2. Physical Dimensions.*—The participation of two guests was much appreciated, since only two of the regular members of the committee were able to be present (A. N. Compton and J. Naghski).

The committee discussed the final form of a draft of the Method for Measurement of Thickness of Units. It was agreed that the method was ready to be submitted to the Committee on Nomenclature and Definitions. This was done.

Dr. Kanagy requested a report on the progress of this Committee in evaluating the available ALCA and KK-L-311a Methods for Physical Dimensions of Leather. We wish to report the following:

1. A tentative Method for Determining Area has appeared as ASTM-D-1515-57T. This embodies ALCA E2 and KK-L-311a, 1121.
2. A tentative Method for Determining Width has appeared as ASTM-D-1516-57T. This embodies ALCA E5 and KK-L-311a, 1211 and 1221.
3. The recently drafted Method for Thickness of Specimens embodies ALCA E4 and KK-L-311a, 1021.
4. The committee is working on a Method for Thickness of Units which will be based on ALCA E3 and KK-L-311a, 1011.
5. At this meeting it was decided to investigate ALCA Methods E2A and KK-L-311a, 1111.

J. NAGHSKI

Section 3. Tensile Properties.—Four members and several guests attended the meeting. ALCA methods E10 through E15 had been approved by the committee, but in reviewing them a few additions were made to make the methods clearer. It was suggested and approved that the Significance sections be written up and submitted for approval. Each member will be asked to submit suggestions for Significance which then will be condensed and written for each method. The data for the Precision section is being processed, and when it is complete, this section will be written up for each method. Data for garment leather will be secured by C. K. Knisely. Malcolm Battles will also be contacted for data on garment leather.

Method E17 (Elongation) was submitted to the meeting for discussion, and copies will be sent to the members not present for their comments and suggestions. It was agreed that it was satisfactory to make one method out of E17 (Elongation), E17a (Alternate Elongation), and Method 2041 (Elongation, Light Materials) from Federal Specification KK-L-311a.

Method 2211 (Resistance to Grain Crack) from KK-L-311a was submitted, and further work will be done on this method within the committee. Three suggestions were made:

1. To compare type of machines for uniformity of the method.
2. To develop a gage to measure distention or stretch of leather as pressure is applied.
3. To compare the test with the Ball Burst Method for Grain Crack.

Method E11 (Buckle Tear) and Method 2121 (Tearing Strength, Splits) from KK-L-311a were discussed as to usefulness. The Joint Committee approved dropping these two methods from the books.

Method E12 (Stitch Tear, Single Hole) was discussed as to the effect, of the size of pin that holds the sample and the space of the yoke to prevent bending of the pin when sample is being pulled. After this has been worked out in the committee, changes will be made also in the specifications of the method. This method can be used for Buckle Tear Strength.

The concordance test on the Ball Burst Method will be run again, since there was a mix-up in the first test. Also the Mullen test will be run on the same samples to see if there is any correlation between the two methods. Both methods will be written up for use in the industry.

It was decided to table all methods from outside groups until after the methods of ALCA have been rewritten and approved by the Joint Committee.

R. L. Young, Jr.

Section 4. Measurement of Water Resistance.—A method for Water Absorption, Static, was submitted to Subcommittee I (R. Lollar) for action, but was retracted later in the day, pending action on a suggested change in the method of calculation from a weight to volume basis in order to present a clearer picture of the water absorption of light-density leathers.

The alternate methods for Water Penetration, Dynamic, were discussed, but are still held up pending further evidence concerning work done by Messrs. Lollar and Maeser.

Dr. Chouinard reported that he has found that the Spray Test gives reasonably concordant results as regards surface characteristics of garment leather and could be written for use on leather substantially as it is now written for textiles. He also considers the Method for Water Absorption on Whole Skins promising and is now engaged in correlation tests in different laboratories.

C. W. Mann reported that the Tap Tester has given satisfactory results on three of five commercial lots of glove leather and that he intended to submit samples soon to other laboratories for correlation.

Dr. Kanagy reported the results on Dynamic Water Absorption by a new test method on samples of crust, finished, and impregnated sole leather from two sources. Arthur Kay is collecting further samples of leathers which will be tested first by Dr. Kanagy and later by Kay and Wagoner on the same apparatus.

Messrs. Kanagy, Mann, and Cooke have volunteered to explore further the Kubelka Method for Static Water Absorption (*JISLTC*, **21**, 9, [1937]) as soon as a source of the apparatus can be located.

Bill Cooke volunteered to furnish some preliminary data regarding the dimensional stability of leather after wetting and drying.

The committee felt the need of a method for measuring the water penetration of finished shoes, particularly those with vulcanized bottoms. Considerable discussion brought out the fact that the Dow Corning Tester did not correlate too well with wear tests. It was agreed to collect more data on the factors influencing correlation of flex and wear tests by engaging the facilities offered by Messrs. Dudley and Mann.

R. G. Ashcraft

Section 5. Leather.—Sixteen members and guests were present during the meeting. Compton noted that the activities of the section were divided into subsections:

1. Lightfastness Evaluation of Leather.—The sample kits for exposure by the various laboratories have been prepared and are almost ready for shipment to the laboratories. However, a few changes in the experiment were made at the meeting, primarily in regard to outdoor exposure, which should consist of two types, one based on Langley units and one based on sun hour units. The other change was from one laboratory method to another.

2. Scuff Resistance of Leather.—Mr. McKee is conducting a survey of section members with regard to methods of scuff testing currently being used. As soon as the survey is complete, an experiment will be initiated studying the various methods and their possible correlation.

3. Crock Resistance of Leather.—Mr. McKee has made a survey of the present methods of determining the crock resistance of leather. It is already apparent that the present ALCA method is not adequate. Experimental work will be required and will be initiated as soon as the survey is completed.

4. Cold Crack Resistance of Upholstery Leather.—C. K. Knisely has prepared a tentative method based on the official method of the Upholstery Leather Group. The method was approved by the section with minor changes. A copy was given to Dr. Lollar, Chairman of Subcommittee I, Nomenclature and Applications. Dr. Lollar's committee has recommended a few revisions in the Significance statement. As soon as this section has been rewritten, it will be submitted to Dr. Thorstensen, Chairman, Subcommittee V, Editorial Committee.

5. *Cold Crack Resistance of Leathers Other than Upholstery.*—A small amount of work has been done studying the applicability of the upholstery leather test to patent leather. This work will be extended and the results reported to the section at its next meeting.

6. *Flex Testing of Finish on Upholstery Leather.*—Mr. Hans Haemisegger prepared a method based on the official method of the Upholstery Leather Group. The method was approved by the section with minor changes. As soon as a Significance section has been added, it will be submitted to Subcommittee I for approval.

7. *Flex Testing of Finish on Upper Leathers.*—Dr. Robert Shaw has completed a survey of the various methods currently used in the industry. It is planned to study these methods and their possible correlation.

8. *Stain Resistance of Leather.*—The Committee assigned to E. D. Compton the responsibility for a survey of methods currently used in the industry.

E. D. Compton
(For R. Stubbings)

Section 6. Fire Resistance.—Inactive.

Section 7. Mechanical Leathers.—Two regular members, one new member, and three guests were present. The object of the meeting was to explore initially the pertinent factors involved in developing a procedure to determine area shrinkage of leather when immersed in various fluids at elevated temperatures. The factors discussed included the size and shape of the specimen; possible fluids such as water, oil, air, and gasoline; the time of immersion required for the specimen to come into equilibrium conditions with the fluid before heating; and the time and temperature of the actual test conditions. It was thought that, for oil, a standard ASTM oil might be used, possibly ASTM No. 1 Oil. It was suggested that commercial hexane would tend to be

more uniform than commercial gasolines. The matters of time and temperature needed additional work and consideration.

The section needs additional "Consumer" representation in order properly to consider some of the factors involved. The matter of section membership was referred to the Advisory Committee. It was suggested that the section chairman examine the ASTM Year Book for potential "consumers" and invite them to join the section. A minimum of ten invitations will be sent out in the hope that the membership can be increased.

A. N. COMPTON

Section 8. Deterioration Effects.—After a review of the various projects within the scope of this section the following action was taken:

1. *Perspiration Exposure.*—Federal Test Method KK-L-311a, 3211, will be compared to the Roddy and Lollar method (*JALCA*, **50**, 180 [1955]). Both white and colored leathers will be evaluated. Laboratory work will be done by the Tanners' Council Research Laboratory, the Eastern Utilization Research Laboratory, and the Dow Corning Corporation.

2. *Heat Stability.*—Both "hot-dry" and "hot-wet" conditions will be investigated. The hot-dry conditions will be 70°C. and 10% relative humidity. The hot-wet conditions will be 70°C. and 90% relative humidity. The Quartermaster Research and Engineering Center, Natick, will conduct evaluation and compare with climatic chamber exposure. As a guide the paper by Roddy and Jansin (*JALCA*, **49**, 773 [1954]) might be useful.

The Bureau of Standards will evaluate the same leather by Federal Test Method KK-L-311a, 3311, which specifies 100°C. and 10% relative humidity for a period of 6 days.

3. *Dry Cleaning Stability.*—A method will be prepared, based upon Federal Test Method CCC-T-191b, 5508. Perchlorethylene will be the solvent, and water and detergent will be added.

C. F. DUDLEY

Section 9.—Disbanded.

Section 10. Miscellaneous Physical Properties.—Six members and a few guests were present. The following methods were considered:

Method E40 (Piping of Upper Leathers). Definition: There seems to be some disagreement as to what piping is. Mr. Bailey held the opinion that piping and coarse break are the same. Others felt that piping showed a tendency for the grain layer to be loosely connected to the under layers so that as the skin is bent with grain inward, there is a tendency for the grain to pull away from the rest of the hide and form its own wrinkles. A clearer definition of piping should be obtained.

Mr. Bailey will send his machine and a number of samples of leather to five laboratories. Each laboratory will determine the number of break lines on each sample. The data will be analyzed to see how closely the laboratories agree.

Piping of Sole Leathers.—The need of a method for measuring the piping of sole leather was seriously questioned. No one from the belting industry was present to explain his attitude toward such a test. It was the consensus of the committee that if a piping test is desirable, it can be made on the same device which is used for measuring the resistance to crack.

Method E41 (Resistance to Grain Cracking).—It was suggested that the English and ALCA methods for measuring cracking should be compared. A small subcommittee should be appointed to do this.

Method E42 (Resistance to Cracking at Low Temperatures).—It was felt that too little was known about the low-temperature uses of leather to attempt to develop proper physical tests at this time. The matter should be brought up at each meeting to see if any tests are necessary.

Method E43 (Stiffness).

Upper Leather.—Maeser showed a drawing of a cheap dead-weight yoke which can be used to determine the stiffness of upper leather. He had a table of results obtained with the yoke. Discs one inch in diameter were folded over, grain out, and placed between the yoke and a flat horizontal surface. The load required to bend the leather to any desired opening can be obtained. The results given in the table were for chrome-tanned upper leather bent until the clear distance between the yoke and supporting bar was three times the thickness of the leather. Several members liked the device. Kanagy will try it out on a number of leathers.

The Pierce Flex Tester was again considered, but Mr. Bailey felt it was good only on thin leathers and soft textiles.

Heavy Leathers.—The committee felt that the present method, using the Olsen Stiffness Tester, should be retained as the official method of the Association. The opinion was expressed that anyone could rig up a simple cantilever beam and hang a weight on the end to measure the stiffness for his own information. Such a method should not, however, be given official recognition.

Method E45 (Compressibility).—Kay sent test samples to Armour Leather Company and A. C. Lawrence Company to be compressed under the conditions of present methods. The final results were not available.

Relative to the problem of indentation hardness vs. compressibility, it was suggested that a subcommittee be appointed to review available data comparing these methods and to bring in recommendations. Need of such a committee will be left up to the chairman.

Kanagy (National Bureau of Standards) is doing work on compressibility and hardness of impregnated leathers. The growing use of such leathers may

make it necessary to change compressibility methods because impregnated leather and regular leather act differently under compression.

Wear Resistance.—At the last meeting (April 1958) Mr. Battles of A. C. Lawrence asked anyone who was making wear tests on sole leather to send samples 1½" x 6" to him so that results obtained on his machine could be compared to wear test results. No samples were received.

In the recent past Kremen is known to have made wear tests on sole leathers. Since he did not attend the meeting, it was suggested that the chairman contact Kremen to see if specimens of his wear test leathers could be supplied to Battles for test.

A number of papers on the abrasion resistance and wear resistance of sole leather were presented at the meeting of Austrian Leather Technologists, Vienna, September 1958 (abstracted *Leder*, **9**, 250–64, 1958). Dr. von Fuchs will call these papers to the chairman's attention.

Run of Glove Leather.—C. W. Mann is trying to develop a test which will correlate with the run of glove leather. He will report again at the next meeting.

Creep of Soling Materials.—Mr. Mann will report at the next meeting on Bauman's device for measuring the creep and spreading of sole leather.

M. Maeser
(For A. N. Kay)

Subcommittee IV. Research.—The meeting was attended by twelve members and four guests.

The first item for discussion was the need for a method for the measurement of comfort in the use of leather. Discussion of what properties might be pertinent to comfort led to the question of how results from such tests could be correlated with a factor as subjective as comfort is. It was agreed that this correlation would be very difficult to establish. However, it was the consensus of the subcommittee that further consideration be given to tests for the cited properties *per se*. These are:

Water vapor absorption from both rate and equilibirium standpoints. (Mann)
Heat conductivity. (Kanagy)
Cyclic stress-strain tensile properties and resiliency. (Lollar)
Electrical conductivity. (Kremen)
Heat of wetting. (Kanagy)

Individual members of the subcommittee who volunteered to look into the possible significance of and general methods applicable to these properties are listed with the respective properties.

Information on tests (SATRA and Lasserre) relative to resistance of leather to dry heat was presented briefly by Dr. Lollar, Mr. Mann, and Dr. von

Fuchs, who will pass their information along to Section 10 which has this property under consideration.

Another Section 10 subject, methods for measuring the wear resistance of sole leather, was discussed briefly. Mr. Kremen will inform Section 10 of a method he has been using and of the availability of samples for correlative tests.

In regard to non-destructive testing, it was suggested that the subcommittee refer to the literature, such as the ASTM bulletins on non-destructive testing, to check on the applicability of any of these tests to leather. The applicability of a Shore Hardness Test to leather was cited as a subject for further consideration.

The subject of leather properties basic to test methods was considered from the viewpoint of determining what properties are being defined in assigning various types of subjective ratings to leather. A list of these rating types, to be supplied by Mr. Bailey, is to be taken under consideration.

The need for a test method for determining the apparent and real density of leather was discussed. The subcommittee recommends that the Advisory Committee consider the adoption of the British official method for determining the apparent density of leather.

M. M. Baldwin

Subcommittee V. Editorial.—During the past six months no methods have been submitted to the subcommittee for editing. The subcommittee is organized and ready to act on any methods as they are prepared by other subcommittees.

Subcommittee chairmen are urged to follow closely the ASTM "Proposed Recommendation on Form of ASTM Methods of Test", dated January 1957, in the preparation of their methods for publication.

T. C. Thorstensen

I.U.L.C.S.

MEETING OF COUNCIL OF DELEGATES

A meeting of the Council of Delegates of the International Union of Leather Chemists Societies was held in the Congress Rooms, via Giolitti, Rome, September 16–17, 1957.

Present were Dr. H. G. Turley in the Chair, the members of the Executive Committee, and 44 delegates representing 13 member societies.

Minutes.—The minutes of the Stockholm meeting were read by the Honorary Secretary and accepted as correct.

Hon. Secretary's report.—The Honorary Secretary presented his report which dealt with the admission of the Indian and Yugoslavian Societies into the Union and the application of the Czechoslovakian Society for admission. It also referred to interest being shown by the U.S.S.R.

Financial report.—The financial report was presented by Professor Burton. After its adoption it was decided to accept the recommendation of the Executive Committee to maintain the subscription for 1958 and 1959 at £6 per official delegate. Dr. Turley made reference to the possibility of increased expenditure principally along the lines of official publication of the proceedings of each Conference. This was being examined, and it was hoped that the proceedings of this Conference would be available early in 1958.

Official language.—It was realized that language difficulties would increase with the growth of the Union. It was agreed that English, French, and German would be the official languages for Conference and committee procedure but that in cases of dispute English would be the referee language.

Admission of Czechoslovakian society.—The admission of the Czechoslovakian Society was unanimously approved. It was pointed out that membership only becomes complete after the payment of dues.

International Council of Tanners.—Dr. Turley stated that the participation of the International Council of Tanners in the Conference was a new departure which he welcomed. Previously they had appealed to the Union for help, even as far back as 1937. The last occasion had been four years ago when a statement had been made on the intrinsic properties of leather. Now he felt the action must be prompt and, if possible, effective. It was hoped to hold talks with the members of the I.C.T. attending the Conference.

International Commission.—Two convenors had found it necessary to resign from their offices: Prof. V. Dumoulin (Leather Analysis) and M. M. Queroix (Tannin Analysis). In the first case Prof. A. Engeler had been recommended, and his appointment was unanimously approved. The Tannin Analysis Commission was discussed. It was felt that practically no improvements in the method had been made in 60 years' work on this subject, and the Union was faced with the problem of finding new principles or abandoning the work of this Commission for the time being. After a vote, it was decided to abandon the Commission.

Standing Technical Committee.—This was not functioning at the moment, and it was recommended that it be abandoned until required, when the personnel necessary to meet the occasion could be appointed. This was approved.

Sampling of vegetable tanning materials.—There was some misunderstanding about the request of the French Society. The matter was referred back for further information.

Election of officers.—Prof. W. Grassmann was proposed as 1st Vice President. This was unanimously approved. The offices of the Hon. Treasurer and Hon. Secretary were both time-expired. Prof. D. Burton was re-elected, and George Forsyth was elected for a period of four years.

Co-opted members.—Four names were put forward for the election of two members. A ballot was taken with the following results:

Dr. P. J. van Vlimmeren	34
Señora M. Paniker de Pelach	23
Dr. H. B. Merrill	22
Dr. Ch. Gastellu	8

Dr. van Vlimmeren and Señora Paniker de Pelach were declared elected.

Venue of 1959 Conference.—Two invitations had been considered by the Executive Committee: Germany and the United States of America. On the recommendation of the Executive Committee it was decided to accept the invitation to hold the 1959 Conference in Germany. Dr. Turley hoped that the still-outstanding invitation to America would be fulfilled in 1961.

Harvey Memorial.—It was decided that a Harvey Memorial Lecture should be presented at the 1959 Conference.

Publication of proceedings.—The Italian Society was attempting to publish the official proceedings of this Conference. Financial assistance from the Union was approved, and it was hoped that this might also be possible for all succeeding Conferences.

Presentation of papers.—A decision of the Executive Committee to allow submitted papers to be read only by authors was agreed on. In the absence of authors, papers would neither be read nor published in the proceedings of the Conference.

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A "special" meeting of the Council of Delegates was held in the Congress Rooms, via Giolitti, Rome, at noon on Friday, September 20, 1957.

Joint Union-I.C.T. Committee.—The President addressed the Council of Delegates on the formation of a joint advisory committee formed from members of the International Union and the International Council of Tanners. He said that it was intended that this committee should be a clearinghouse, to check information going out to the propaganda people. It was to come into being in the first instance as an advisory committee with equal representation on both sides. The ideal composition would be:

2 publicists
2 tanners
2 chemists from the Industry
2 research chemists

The initial work would be concerned with publicity, but it was hoped as time went on this committee would be able to advise on possible improvements in leather. Various views were expressed by the meeting, concerning the existence of a Leather Improvement Society, the danger of overloading the committee with chemists, and queries regarding the "terms of reference" of such a body.

A proposition was put forward "That the Executive Committee shall put in writing formal proposals for cooperation with the tanners on behalf of leather and circulate this to all member-societies for consideration". After some discussion it was suggested that this would cause long delay and immediate action should be taken. A vote was taken and the proposition was defeated by 25 votes to 14.

Five names were put forward to form the nucleus of the committee:

Prof. W. Grassmann
Dr. K. W. Pepper
Dr. A. Simoncini
Prof. D. Burton
Mr. J. Mallebay

On a proposition by E. B. Thorstensen it was agreed to empower the Executive Committee to appoint the remaining members. An undertaking was given to keep all member-societies supplied with information regarding the activities of this joint committee.

ABSTRACTS

Leather Industries Research in Czechoslovakia. L. Masner. *J. Soc. Leather Trades' Chemists*, **42**, 335–41 (1958).—A description of leather science and technology in Czechoslovakia. J.M.C.

Zirconium Tannage. I. A Colorimetric Method for the Determination of Zirconium in Leather. D. A. Williams-Wynn. *J. Soc. Leather Trades' Chemists*, **42**, 360–68 (1958).—Solubilization of the leather is accomplished by wet oxidation ($HClO_4$, H_2SO_4, HNO_3 mixture). After dilution aliquots are transferred to volumetric flasks containing *N*HCl. Alizarin-S and sodium tartrate are added; the latter has been found to reduce the extremely intense color and to stabilize the system against precipitation. The flasks are heated in boiling water to provide optically clear solutions, cooled, made to volume with water, and the absorbance determined at 520 mμ. Ti, Al, Fe, and Cr^{+++} do not interfere. Hexavalent Cr must be reduced before taking aliquots for color development. The method is shown to give results equivalent to those obtained by a standard gravimetric procedure. J.M.C.

Studies on Zirconium Tannage. The Mechanism of the Tannage. T. S. Ranganathan and R. Reed. *J. Soc. Leather Trades' Chemists*, **42**, 351–60 (1958).—Experiments in which deaminated, methylated, and standard hide powders were tanned with $ZrSO_4$-type salts indicate that fixation of Zr depends to some extent on protein amino groups but is independent of carboxyl groups. The Zr metallic complex is also apparently fixed by the hide powder through mechanisms such as hydrogen bonding and physical deposition of Zr compounds. By experimenting with combination Zr and Cr tannages it is shown that Zr and Cr are fixed in the protein by relatively independent mechanisms. J.M.C.

Relation between the Structure and the Technical Characteristics of Anionic Dyes. I. Mustea. *Ind. Usoara* (Bucharest), **5**, 207–10 (1958); *Chem. Abstr.*, **53**, 720*h*. **The Influence of Sulfonic Groups in the Reaction between Dye and Leather.** *Ibid.*, 298–305; *Chem. Abstr.*, **53**, 750*c*.

Cross-linking of Gelatin under the Influence of Heat. J. Bello and H. Reise-Bello. *Sci. et Inds. Phot.*, **29**, 361–64 (1958); *Chem. Abstr.*, **53**, 109*a*.

Examination of the Structure of the Collagen Tissue. J. Balo, I. Banga, and D. Szabo. *Magyar Tudomanyos Akad. Biol. es Orvosi Tudomanyok Osztalyanak Kozlemenyei*, **7**, 385–410 (1956); *Chem. Abstr.*, **53**, 467*h*.

Elastin. Products of Partial Alkaline Hydrolysis. L. Gotte and V. Moret. *Atti Accad. Nazl. Lincei Rend., Classe Sci. Fis., Mat. e Nat.*, **24**, 321–25 (1958); *Chem. Abstr.*, **53**, 481*b*.

Complexometric Titration of Chromium(III) Ion in Chromic Acid Solution. R. Weiner and E. Ney. *Z. Anal Chem.*, **161**, 432–33 (1958); *Chem. Abstr.*, **53**, 124*e*.

Determination of Zirconium with the Aid of Ammonium Benzene- or Napthaleneseleninate. I. P. Alimarin and V. S. Sotnikov. *Zhur. Anal. Khim.*, **13,** 332–36 (1958); *Chem. Abstr.*, **53,** 130*d*.

The Acid Mucopolysaccharides of Connective Tissue. III. The Sulfate Linkage. P. Hoffman, A. Linker, and K. Meyer. *Biochim. Biophys. Acta.*, **30,** 184–85 (1958).—Confirmation is provided for a previous suggestion that chondroitin sulfate B contains galactosamine-4-sulfate and that spectral differences are due to the presence of C-4 and C-6 sulfate esters in the galactosamine moieties of chondroitin A and C respectively. J.M.C.

The Soluble Proteins of Bovine Hide. II. Extraction by Aqueous Sodium Phosphate and Half-saturated Lime. D. R. Cooper and P. Johnson. *Biochim. Biophys. Acta.*, **30,** 590–97 (1958).—Detailed description is given of the two extraction procedures studied. Exhaustive phosphate extraction of hide, previously extracted with NaCl-solution, produced only 0.3% extractable nitrogen. Extraction of hide corium gave results which did not differ significantly from those obtained on whole hide. Although similar in some respects, phosphate and NaCl-solution extracts are significantly different. The lower N content of the phosphate extract indicates the presence of larger amounts of nonprotein conjugation material. i.e., hyaluronic acid. The bulk of the nondialyzable material extracted with phosphate solution is not of a collagen type. In general, the phosphate-extracted material is very similar electrophoretically to that extracted by salt and to bovine serum. Lime extracts of hides contained mainly the same components as the saline and phosphate extracts though in different proportions. J.M.C.

Comparative Biochemistry of Collagen. Some Amino Acids and Carbohydrates. J. Gross, B. Dumsha, and N. Glazer. *Biochim. Biophys. Acta*, **30,** 293–97 (1958).—A comparison is made of the tyrosine, glycine, proline, and hydroxyproline as well as sugar content of collagen and gelatin derivatives from mammal, fish, echinoderm, coelenterate, and sponge. Amino sugars were separated, prior to analysis, by ion exchange and were identified by paper chromatography. All materials yielded the typical wide-angle X-ray diffraction pattern. The relative proportions of glycine, hydroxyproline, and proline are of the same order of magnitude for all collagens reported. The large variety of sugars associated with the collagens suggest that if the carbohydrate is in polysaccharide form, there is probably more than one molecular species present. J.M.C.

A Review of the Literature of 1957 on Sewage, Waste Treatment, and Water Pollution. II. H. Heukelekian *et al. Sewage and Ind. Wastes*, **30,** 717 (1958)—The following literature references pertaining to tannery wastes are cited: (1) Eick ("Tannery Wastes Disposal by Spray Irrigation", *Ind. Wastes*, **1,** 271 [1956]; abstracted JALCA, **54,** 53 [1957]); (2) Berg, K. ("Design Basis for the Treatment of Sewage from Factories of the Leather Industries". *Wasser- u. Boden*, **8,** 340 [1956]; *Literaturberichte*, **5,** 460 [1956]); (3) Kubelka and Holamek ("Final Purification of Tannery Effluents",

Kozarstvi, **6**, 93 [1956]; *Chem. Abstr.*, **51**, 9191 [1957]). They reported results of experiments on various methods of tannery waste treatment. They found that plain sedimentation is usually not adequate treatment. Coagulation with alum and sulfuric acid at pH 7.0 gave better results. Treatment with $FeSo_4$ without neutralization is possible only if the waste is first oxidized with chlorine. The sludge produced from these processes can be dried on beds and contains 10% CaO and 2 to 3% N. The sludge cannot be burned but can be used as a fertilizer after mixing with manure and storing for several months to decompose the tannin. Anthrax spores settle out in the sludge and are destroyed or inactivated by this treament. J.F.W.

The Insolubilization of the Tannin Not Chemically Fixed to the Dermic Fiber, in the Vegetable Tanning of Sole Leather. G. Alexa, C. Strub, I. Iarosinski-Drabic, and C. Maga. *Cuoio, pelli, mat. concianti*, **34**, 136–48 (1958).—The yield of sole leather may be increased if the free tannin (free, washable, or combined but easily hydrolyzable) is insolubilized with HCHO or analogous compounds. Several samples of leather tanned with oak, spruce, quebracho, and valonea extracts show a decrease of the percentage of soluble matter from 25–30% to 7–11% after treatment with HCHO. There is no relationship between the strength and the amount of tannin insolubilized during this retanning with HCHO, but the absorption of water and permeability are noticeably decreased by the treatment. The retanning may be made by treating the vegetable-tanned leathers with a 1% solution (calculated on the hide weight) of commercial HCHO (30%). The excess of HCHO remaining in the hides should be neutralized by a rapid treatment with a tannin solution. G.A.B.

Rapid Oven-Drying in Leather Analysis. A. Jamet and P. Bourgeat. *Cuoio, pelli, mat. concianti*, **34**, 45–47 (1958).—An oven for the rapid drying of the total soluble matter and total solid matter in tannin analysis was previously developed and adopted by the French Society of Leather Chemists. Rapid drying is obtained by passing a current of dry heated air through the oven. This method has now been applied to the determination of moisture in leather. The time necessary to reach constant weight is only 15 min., and the results are practically identical with those obtained by the Official Method (drying at 104°C. for several hours). G.A.B.

The Problem of Sewage Waters in Italy: Laws and Methods of Control and of Purification. L. Del Pezzo and A. Simoncini. *Cuoio, pelli, mat. concianti*, **34**, 196–207, 285–95 (1958).—Besides the general laws concerning the discharge of the town waters into the rivers and canals, there are in Italy some special laws to regulate tannery waters, which must be submitted to a purification process able to avoid any possibility of diffusion of infections, particularly anthrax. The control is made by the officers of the sanitary departments of the towns and provinces. The ordinary purification system is based on a series of decantation pits, sand filters, treatments with Cl_2, etc., and only after a severe control can the waters be discharged into the rivers. The tannery residues contain, on the average, per 100 kg. of raw hides, 30 kg. of hair, fleshings, shavings, soluble protein hydrolyzate, etc. These residues are partially utilized for the manufacture of glue, felts, fertilizers, etc. The volume of the

water discharge is 5–7 cu. m. per 100 kg. hides. The waters coming from the various tannery operations show the following average composition:

	Total Solids g/l	Soluble Matter g/l	Suspended Matter g/l	B.O.D. g. O_2 per l. after 5 Days	pH	Volume %
Soaking	12	11.0	1.0	1.0	6.2	12
Liming	25	17.5	7.5	2.5	11–12	17
Deliming, bating	4	3.8	0.2	0.3	8	12
Pickling, pretanning	60	59.0	1.0	0.8	2.5	5
Vegetable tanning	19	17.5	1.5	6.0	4–5	5
Chrome tanning	78	75.5	2.5	0.5	3	10
Fatliquoring, dyeing	2	1.7	0.3	0.3	4	39
General washing						
						100

The waters from the first to fifth treatment have a putrid smell. Some of the chemicals contained in these liquids may be toxic to living organisms, because the limits of toxic values are approximately: 0.7% CaO, 1% tannin, 0.5% Cr salts, and 0.01% H_2S. Moreover, some waters may contain pathogenic microorganisms and anthrax spores. By mixing together all the waters of a tannery, there is a flocculation of the colloidal suspended matters, and reciprocal neutralization of the acids and alkalis (generally an excess of alkalinity is found after the neutralization), but by this procedure the volume of the liquids to be purified is very great. The wash waters (about 39% of the total volume) need not be purified in any way, as their B.O.D. is nil. A complete treatment of the tannery waters may include a preliminary coarse filtration to separate the suspended matters, a decantation in pits for a first sedimentation, and the introduction of chimney gases into the liquid (in another series of pits), which neutralizes and precipitates CaO and flocculates the protein colloids. The waters from soaking, deliming, and bating, and the other wash waters (in total, 63% of the volume) are only filtered and decanted. The liming waters may be treated with various chemicals (SO_2, $FeCl_3$, alum, hypochlorite, etc.) but the most convenient treatment is that with $FeSO_4$. In a tannery discarding 110 cu.m. waters daily the consumption of $FeSO_4$ is about 90 kg. and may be reduced if H_2S is partially oxidized by blowing in air or by agitation. The waters from tanning, fatliquoring, and dyeing are not filtered but only allowed to settle for a sufficient time, then mixed with the ordinary wash waters. The control of the sewage waters should be made frequently, and it is necessary to determine temperature, color, smell, pH, suspended matter, residue at 100° and at 600°, B.O.D., oxidizability, dissolved O_2, N, Cl, SO_4, and Ca. G.A.B.

Preliminary Researches on Several Tannin Fractions Obtained from Indian Plant Tanstuffs. S. K. Barat. *Cuoio, pelli, mat. concianti,* **34,** 223–30 (1958).—Barks of goran (*Ceriops roxburghiana*) and sonali (*Cassia fistula*) together with myrobalans and wattle were extracted with $(CH_3)_2CO$; the ex-

tract was dried *in vacuo*, then dissolved in H_2O; and the insoluble matter was determined. The H_2O solution was shaken with ethyl acetate at various pH values. Samples of pelts were tanned with the tannins obtained in these fractions. The shrinkage temperature and the tanning index were determined, and the "gelatin number" was determined on the same solutions. Gelatin number = parts by weight of tannin combined with 100 parts of gelatin, and its value for the ethyl acetate extracts at pH 7 and at pH 1 and for the insoluble fraction, was resp.: myrobalans, 143, 88, 180; goran 136, 137, 215; sonali 133, —, 61; and wattle 115, 181, 70. The method of determination of the gelatin number is the following: 1 g. gelatin is dissolved in distilled H_2O at 45°C., cooled, and added to 200 ml. of filtered solution containing 6 g. tannin, shaken for 5 min., and let stand for 1 hr. The precipitate is filtered through a Buchner funnel, washed 6 times, and dried in a desiccator *in vacuo*, then in an oven at 105°C. Gelatin in the dried precipitate is determined by the Kjeldahl method, and the weight of tannin is calculated by difference. G.A.B.

Chelating Agents in the Decolorization of Chestnut Extracts. A. Simoncini. *Cuoio, pelli, mat. concianti*, **34**, 93–118 (1958).—Chestnut wood contains an average of 0.4 mg. Cu and 1 mg. Fe per 100 g. (on dry basis); tanning extracts contain an average of 50–100 p.p.m. Fe and various amounts of Cu, depending on the method employed in the extraction of the vegetable matter. To avoid the action of these metals (formation of spots of Cu or Fe tannate, catalysis of oxidation phenomena, etc.) many methods have been proposed, and good results were obtained with the chelating agents. The action of ethylenediamine tetraacetic acid or its Na salt (EDTA) was examined by measuring the color of the extracts (with the Lovibond Tintometer) containing increasing amounts of Fe, and the color of leathers tanned with the said extracts. The chelating activity is proportional to the amount of added EDTA and to the percent of Fe in the extract, but it is not possible to chelate the total amount of Fe present, because in the extracts there is free (ionic) Fe and Fe combined with the tannin molecule. Only the first may be eliminated by chelation—not the latter, even if the combination with tannin is labile. Extracts treated with EDTA or leather washed with a solution of EDTA may be noticeably decolorized, but the best results are generally obtained by adding EDTA in the tanning pits. G.A.B.

Methods of Analysis Used in the Experimental Station for the Leather Industries in Naples (Italy). *Cuoio, pelli, mat. concianti*, **33**, 203–30, 281–305, 469–81, 541–57 (1957); **34**, 48–57, 151–55, 231–45 (1958). —The following methods are described: Chemical analysis of leather: sampling, qualitative research on the tannin used, H_2O, ash (Mg, Ca, Ba determinations), fatty matter (saponification no. and unsaponifiable matter), soluble matter (Koch extraction, shake method, Swiss method, soluble nontannins), reducing sugars, insoluble ash, hide substance, fixed tannin, pH (and difference figure), Procter-Searle index, buffer index, degree of tannage, yield degree, nomograms for reducing the results at a standard H_2O content; analysis of chrome leather, fats and free S ($CHCl_3$ extraction), Cr (alkaline decomposition), Cr (wet oxidation), Fe and Al, total chlorides, total and combined sulfates, basicity of the leather, Al in alum-tanned leather, Fe in iron-tanned leather, SiO_2 and Zr in zirconium-tanned leather; analysis of chamois leather, determination of

fixed fats; determination of Cr in leather which ordinarily should not contain Cr; determination of cellulose; bacteriological examination, resistance of leather to *Aspergillus niger* and to a mixture of fungus spores prepared on purpose. G.A.B.

Contribution to the Knowledge of Oil Tannage. R. Airoldi. *Chimica e Ind.* (Milan), **40,** 634 (1958).—Chamois (oil) tannage may be explained by the following hypotheses: (1) the highly unsaturated fatty acids or their glycerides are oxidized with formation of peroxides or hydroxy derivatives which are able to combine with collagen; the reacting groups of the peptide chain are presumably -CO-NH-; (2) the said fatty acids are transformed into peroxides and aldehydes, and among these acrylic aldehyde particularly may react with NH_2 groups of collagen. The hypothesis that some polymerization products of the fatty acids form a protective sheath around the fibrils was not confirmed by the electron-microscopical examination of both a hide and oil-tanned fibrils: the latter does not show any sheath. Several samples of oil-tanned leathers were analyzed, and extraction with organic solvents was made before and after destruction of the hide substance (boiling the leather with an alcoholic solution of NaOH). The results obtained by direct determination of fatty matter after destruction of the hide substance (i.e., determination of the products soluble in C_2H_5OH and in $(C_2H_5)_2O$) correspond to only 50–70% of the values found in the usual analysis by difference as "combined fatty matter". It is probable that in oil tannage there is not only the combination with collagen of a unique compound or group of similar compounds, and therefore it is suggested that the determination of the combined fatty matter is made by difference between 100 and the sum of the other constituents (moisture, ash, fatty matter soluble in petroleum ether, fatty matter soluble in a mixture (1:1) of C_2H_5OH and $(C_2H_5)_2O$, and hide substance). For the calculation of the percent of hide substance, the percent of nitrogen is to be multiplied by the factor 5.85 for sheepskin and 5.62 for calfskin. G.A.B.

Pleomorphism by Vegetable Tannins. A. Simoncini. *Cuoio, pelli, mat. concianti,* **34,** 339–71 (1958).—It is well known that microorganisms grow by direct division, i.e., the dimensions of a cell increase, and then it divides in two, and so on, following a growth law which is called the "logarithmic phase"; the daughter-cells show the same characters as the mother-cell. In some cases the cell grows without dividing and forms giant cells showing modified properties; this phenomenon is called "pleomorphism" and may be spontaneous (e.g., in some aged culture media) or provoked by the addition to the medium of some substances (LiCl, EtOH, detergents, urethan, colchicine, indole, camphor, amines etc.). Several tannins were tested on their ability to provoke the pleomorphism of *Escherichia coli.* The experiments were made with tannic, gallic, and ellagic acids, and with extracts of wattle, quebracho, algarobilla, chestnut, eucalyptus, gambier, oak, and sumac. Examination of the microscopic preparates was made up to 144 hr. at 25°C. and 37°C. All the products examined (excepting ellagic acid) show the ability to induce the formation of filamentous forms of the microorganism; the total number of these filamentous forms in the case of sumac extract reaches 100%, and their length, which is about 1–1.5 μ in the original cells, increases even to 400 μ. The maximum of action was observed at pH 7.2; at pH 5.5–

6.5 only a few cells have a filamentous or a clavate shape, and at pH less than 4.5 the growth is inhibited. The hypothesis of a possible defect in the synthesis of protein matter by the bacterial cells in the presence of tannins is discussed. There are 65 references. G.A.B.

The Molecular Weight of Black Wattle Tannins. IV. The Fractional Extraction of Fresh and Commercial Bark Samples. S. R. Evelyn. *J. Soc. Leather Trades' Chemists*, **42**, 282–88 (1958).—The polyphenols dissolved by the initial cold leach of dry chip bark are of higher molecular weight than the polyphenols dissolved by subsequent hot water extraction. Fractionation of fresh bark by successive extraction with solvents of progressively increasing polarity showed that ethyl acetate dissolves the low-molecular-weight polyphenols while subsequent ethanol and methanol leaches extract the more condensed tannins. The presence of moisture in fresh bark is responsible for enhanced solubility of more condensed polyphenols in either methanol or ethanol. The major portion of wattle tannin polyphenols examined had molecular weights ranging from 900 to 1600. J.M.C.

Report of the Committee on Colorfastness to Washing of the American Association of Textile Chemists and Colorists. R. B. Smith, Chairman. *Am. Dyestuff Reptr.*, **48**, 18–20 (1959).—The work of the committee on accelerated washfastness tests in home and in industrial laundering is described. C.L.D.

Mechanism of Formation of Anthocyanidins from Leucoanthocyani(di)ns. D. G. Roux and M. C. Bill. *Nature*, **183**, 42 (1959).—Leucoanthocyanins (previously shown to be possible precursors of tannins) are converted into anthocyanidins in greater yield and more rapidly if they are treated with HCl in propan-2-ol under anhydrous conditions, instead of with aqueous HCl in the same solvent. These facts support the theory that the initial step in the reaction is a dehydration. Implication of these findings for the chemistry of condensed tannins will be discussed in a later paper. C.L.D.

Detection of Antibacterial Property of Fabrics—Agar Plate Method. Committee of Antibacterial Agents of the American Association of Textile Chemists and Colorists. I. Schwartz, Chairman. *Am. Dyestuff Reptr.*, **48**, 8–9 (1959).—Specifications are given for a tentative test method in which the fabric is placed on the surface of agar seeded with a standard strain of *Micrococcus pyogenes* var. *aureus* and then incubated. C.L.D.

Report of the Committee on Colorfastness to Light of the American Association of Textile Chemists and Colorists. J. E. Norton, Chairman. *Am. Dyestuff Reptr.*, **48**, 12–13 (1959).—Work of the committee on the sunlight and daylight test methods, on laboratory methods and their correlation with natural light tests, on the combined effects of light and atmospheric contaminants, and on the colorfastness to weathering of textiles is described. C.L.D.

Report of the Committee on Drycleaning Test Methods of the American Association of Textile Chemists and Colorists. A. E. Johnson, Chairman. *Am. Dyestuff Reptr.*, **48**, 17–18 (1959).—The use of perchloroethylene (to replace CCl_4) in the drycleaning test, the effect of higher solvent temperature in the test, and shrinkage in drycleaning are discussed. C.L.D.

The Behavior toward Water of Vegetable-Syntan-tanned Leather. G. Reich and F. Stather. *Das Leder*, **9**, 249–53 (1958).—German (Eastern Zone) sole leather is now tanned in blends containing from 50 to 100% syntan. Since 1942 there has been a steady increase in water absorption value of the leather and a decrease in moisture content after storage. This apparently contradictory condition is of practical importance. A study of water vapor take-up was made using portions of unchromed Freiberg hide powder after tanning them with syntans or vegetable extracts. The degree of tannage was varied by using 30, 60, 110, or 160% of available tannin (percentage of pure tannin available to the hide) in the tanning liquors. The tanned powders were thoroughly washed, dried in a current of air, then exposed at 20°C. in desiccators to an atmosphere saturated with water vapor until equilibrium was reached. Then they were weighed, and the increase in weight was determined. Moisture was determined in a separate portion of the material, and this value was used in the calculation of total water take-up. The results are shown in the following table:

Tanning Material	Degree of Tannage	Maximum Water Uptake		Water Absorption	
		Leather Basis, %	Hide Substance Basis, %	Leather Basis, %	Hide Substance Basis, %
Spruce	17.5	55	65	236	360
	28	50	65	177	300
	39	47	65	157	280
	59	41	65	115	270
Oak	20	52	63	204	300
	37	50	68	155	255
	59	40	64	131	255
	64	35	57	127	265
Pellutan EZE	17.5	47	55	203	285
	28	45	58	183	285
	39	39	54	188	310
	47	38	56	168	320
Pellutan G-40	22	46	56	192	235
	35	43	58	180	245
	43	39	55	136	195
	56	32	50	208	352

The above data show that water vapor absorption decreased as the degree of tannage increased, but that on the hide substance basis it was essentially constant for a given tanning material. Vegetable-tanned leather powders took up more water vapor than syntan leathers; this was also true when the leathers were exposed to relative humidities below 100% and at different temperatures. The

following table shows water vapor absorption values expressed as percentages of hide substance:

Tanning Material	Degree of Tannage	Temp. °C.	Relative Humidity, %				
			37	58	70	80	94
		20	10	17	23	27	37
Spruce	28	40	8	15	17	19	21
		60	3	12	12	18	—
		20	8	17	25	28	38
Oak	37	40	7	15	17	18	23
		60	3	11	18	17	—
		20	7	14	19	23	34
Pellutan EZE	28	40	6	12	14	16	19
		60	4	10	10	15	—
		20	8	15	22	26	36
Pellutan G-40	35	40	7	13	14	17	20
		60	3	10	11	13	—

The hygroscopic behavior of certain tanning materials and of the nontannin fraction of these materials (filter method) was investigated by exposing dried residues for 3 days in a desiccator saturated with water vapor and weighing to find the amount of water absorbed. The percentages (dry tanning material basis) of water vapor absorbed and the percentages of these values absorbed by the nontannin were respectively as follows: wattle 145, 40; oak 147, 91; sulfited quebracho 153, 100; spruce 156, 85; Pellutan G-40 170, 100; Pellutan EZE 178, 58; Wofagan E 178, 81; and Wofagan M 185, 70. The nontannin of quebracho and Pellutan G-40 was responsible for all of the water taken up by these materials, and the tannin was responsible for none. Water absorption of the leather powders was also measured, and the results are shown in the last 2 columns of the first table above. Water absorption of vegetable leather decreased to a minimum, then remained constant as the degree of tannage increased, but absorption of syntan leather first decreased, then rose sharply. Syntans, which have sulfo groups, react with free amino groups of the hide, reduce the ability of the hide to swell, and therefore reduce water absorption. If, however, the syntan content of the leather is high, free sulfo groups are present and they increase the absorption of water but not of water vapor. Syntan leathers absorbed more water than a standard vegetable leather; most of the difference was in bound water, as capillary water was only slightly higher. Data on heat of wetting were not helpful in reaching conclusions regarding either water vapor absorption or the affinity of the leather for water. I.D.C.

A New Tester for Investigating and Evaluating the Water Resistance of Shoes and Sole Leather. P. Kontio. *Das Leder*, **9**, 246–49 (1958). —A "walking machine" made in Helsinki, Finland, and designed for testing shoes and sole leather, is described. The test shoe is placed over a last attached to the bottom of a vertical rod which is moved up and down by a motor-driven eccentric (31.5 rpm). The last is hollow so that water from a thermostat-controlled bath can be circulated through it to heat the inside of the shoe during studies on the sweat resistance of insoles. As the shoe moves down it

comes in contact with a special surface in a pan. A lever with an adjustable weight is attached to the bottom of the pan so that a pressure of between 30 and 80 kg. is exerted on the shoe. The pan should contain enough water to cover the shoe sole; the special surface may be cement, brick, asphalt, sand, or other material. A metal plate (and steel wool) inside the shoe is connected to a relay circuit with a resistance up to 15×10^6 ohms, so that the machine is stopped when water first penetrates the shoe. Sole leather is tested by replacing the last with a 5 x 5 cm. metal plate which periodically exerts a force on the leather specimen resting in the pan. The machine can also be used to determine wear resistance, sweat resistance, point of penetration of water, etc. Water penetration values found by the machine were in excellent agreement with those found by actual wearing of the shoes in a water-covered cement canal. I.D.C.

Determination of the Water Penetration of Leather. R. Stratta. *Das Leder*, **9**, 229–30 (1958).—Dynamic methods must be used to measure the resistance of leather to water; static methods are not practical enough. An apparatus for determining permeability to liquids or gases consists of two cylindrical chambers (diameter 69 mm.) between which the leather specimen is clamped at its edge. Pistons are mounted through bushings in the center of each chamber so that the center of the leather specimen can be forced to vibrate back and forth. One chamber has inlets through which liquid or gas can be introduced under pressure. The other chamber has a Plexiglass window and also electrical contacts for determining the time of pentration of a conducting liquid. It is possible to vary pressure, speed of piston, and size of piston head. Time for penetration (minutes) should be reported rather than number of strokes of the piston. Results with this machine were in good agreement with those by the Bally Penetrometer and the Baumann Sole Leather Penetrometer. I.D.C.

Sumac in Sicily. A. Annunziata. *Das Leder*, **9**, 254–57 (1958).—A brief, general description of cultivated sumac. I.D.C.

Collagen in Human Cementum as Shown by Electron Microscopy. C. H. Tonge and E. H. Boult. *Nature*, **182**, 459–60 (1958). R.M.L.

The Nature of Permanent Set in Keratin Fibers. M. Feughelman, A. R. Haly, and T. R. Mitchell. *Textile Research J.*, **28**, 655–59 (1958).—Permanent set of keratin fibers in water has been shown in the past to be mainly due to strong polar linkages formed during the process. This paper identifies these linkages with the bonds broken in the second stage of supercontraction of a fiber in concentrated LiBr solution; these bonds are probably formed by groups of cooperative hydrogen bonds associated with a tyrosine residue in the keratin structure. R.M.L.

Spectrophotometric Determination of Protein and Total Carbohydrate. B. R. Hewitt. *Nature*, **182**, 246–47 (1958).—The protein method permits the determination of protein in alkaline solution by a modification of the

Folin phenol reagent, while the total carbohydrate method uses anthrone as the reagent. The first method has a duplicate sample error within 5%, while the carbohydrate method shows a duplicate sample error less than 8%. R.M.L.

Effect of Neutral Salts on the Structure of Collagen and Gelatin. W. F. Harrington. *Nature*, **181,** 997–98 (1958).—The similarity between the effects of heat and neutral salts in contracting the collagen fibrils suggests that the shrinkage behavior of collagen at elevated temperatures in the absence of salt, and at low temperatures in the presence of salt, could be strongly dependent on trans-cis isomerizations at the proline-proline peptide bonds. R.M.L.

^{14}C-Proline and Hydroxyproline in the Protein Metabolism of Plants. F. C. Steward and J. K. Pollard. *Nature*, **182,** 828–32 (1958).—A discussion of certain examples in plants in which ^{14}C-proline is directly and rapidly incorporated in a metabolically inactive plant protein (insoluble in alcohol, precipitable with trichloracetic acid) and then progressively converted to bound hydroxy-*l*-proline. R.M.L.

Submicroscopic Structure of Elastic Fibers as Observed in the Polarization Microscope. G. Romhanyi. *Nature*, **182,** 929–30 (1958).—The structural pattern of the elastic fibers suggested on the basis of this study is in agreement with Hall's model, which is based upon electron microscopic and chemical evidence. However, polarization microscopy has shown that, apart from their inner spiral achitecture, a considerable portion of the mucoid component of the elastin fibers is not amorphous but longitudinally oriented along the fibers. This may possibly result from an interaction of the mucoid component with the protein filaments arranged longitudinally. R.M.L.

Protein Hydration and Behavior. I. M. Klotz. *Science*, **128,** 815–22 (1958).—Several unique features of protein behavior, emphasizing those related to the uptake of protons by the protein molecules, have been re-examined. A thread of likeness can be drawn through these features when the hydration sheath is viewed as an icelike lattice. Interpretation of the behavior of the protein emphasizes the important role played by the solvent in fixing the structure and properties of the solute molecule as well as the influence of the solute in imposing a structure on the solvent. This mutual interaction has perhaps not been fully appreciated in interpretation of the behavior of proteins in solution. R.M.L.

Leucoanthocyanins as the Possible Precursors of Tannins. W. E. Hillis and G. Urbach. *Nature*, **182,** 657–58 (1958).—Recent publications have suggested that condensed tannins have either leucoanthocyanins or catechin as precursors. It has been found that the HCHO uptake of catechin polymer and catechin decreased on heating, while with the tannin extracts it increased. Catechin polymer does not react with vanillin-HCl as the tannins examined do. Spectral data also indicate the dissimilarity of catechin polymer and the tannins. **Formation of Condensed Tannins in Plants.** W. E. Hillis. *Ibid.*, 1371 (1958).—The evidence indicates that the glycoside moieties are metabolized in the living cells of sapwood, particularly in the region of increased activity at

the heartwood boundary. Leucoanthocyanins appear to be a common product of this metabolism. Recently it was found that the amount of (+)-catechin was much lower in the heartwood than in the sapwood of species which also contained the leucoanthocyanins. Consequently, it seems likely that the condensed tannins in many woody plants are formed by the polymerization of leucoanthocyanins, either alone or in conjuction with catechin and other components. R.M.L.

Attempts to Introduce Amide Cross Links into Wool. J. A. McLaren. *Textile Research J.*, **28,** 946–48 (1958).—Wool which has been modified with biscyclohexyl carbodi-imide is almost unchanged in weight, handle, and appearance but has increased resistance to attack by alkali, alkaline thioglycollate, urea-bisulfite, and trypsin. **II. The Alkaline Thioglycollate Extraction Test for Wool.** F. G. Lennox. *Ibid.*, 949 (1958).—The details of a routine test method are given. R.M.L.

Influence of Time on the Reversible Association between Large Molecules. The Collagen System. J. Gross. *Nature*, **181,** 556 (1958).—Cold neutral salt extracts of fresh skins from growing animals contain collagen in solution which may be precipitated as an opaque gel composed of cross-striated fibers, characteristic of the native tissue, on warming to 37° C. The opaque collagen gels occasionally redissolve on cooling in the refrigerator. Increased time of holding at 37° from 10 min. to 48 hr. decreases the opacity loss by the gels upon cooling, so that the 48-hr. incubation produces a gel which loses only 10% of its opacity at 37° when cooled to 2° C. R.M.L.

A Comparison of Three Methods for the Determination of Tearing Strength of Fabrics. L. H. Turl. *Textile Research J.*, **28,** 839–48 (1958).—Three standard tearing tests for use on fabrics (single rip, wing rip, and tongue tear test) have been critically compared and found to measure the same fabric property. A modification of the wing rip test to make the method more widely applicable is suggested in place of these 3 methods. R.M.L.

Mucopolysaccharides of Costal Cartilage. K. Meyer, P. Hoffman, and A. Linker. *Science*, **128,** 896 (1958).—Keratosulfate, a polymer of unknown structure composed of equimolar amounts of N-acetyl glucosamine, galactose, and sulfate, may be more widely distributed in connective tissue than has been believed heretofore; the solubility of its salts in alcohol may be the cause of its presence not being detected. The distribution of keratosulfate and of the types of chondroitin sulfate will have to be reinvestigated. R.M.L.

"Purity" of Gelatin as a Protein. G. Russell. *Nature*, **181,** 102–3 (1958).—High-grade, lime-processed gelatins, with isoelectric points in the region of pH 5, have been divided into two fractions by the use of column chromatographic techniques, using Amberlite XE-97. pH differences during elution yielded the two fractions which differed significantly in their tyrosine content. Implications of the finding are many. It may be that either an interprotein

complex or a definite impurity of possibly variable concentration is present. The implication of the latter possibility to such studies as N-terminal amino acid groups, gelatin structure, and amino acid sequence is noted. R.M.L.

Variation with Age of Shrinkage Temperature of Human Collagen. Patricia C. Brown and R. Consden. *Nature*, **181**, 349–50 (1958).—The shrinkage temperature (micromethod) of collagenous fibers teased from human *dura mater* or *fascia lata* was found to increase with the age of the individual at the time of death. R.M.L.

The Alpha-Beta Transformation in Keratin. A. R. B. Skertchly. *Nature*, **181**, 639–40 (1958).— A quantitative X-ray investigation of the transformation in Lincoln wool keratin permits the deduction that the reaction proceeds through an intermediate β^* phase of less order than either the alpha or beta phases. The alpha phase which represents approximately 60% of the fiber is in series with a less extensible gamma phase, which phase requires severe disulfide bond rupture to enable it to be strained. R.M.L.

Tryptophan Content of Wool. D. R. Graham and K. W. Statham. *Nature*, **181**, 861 (1958).—The tryptophan contents of the keratin samples examined lie between 0.5 and 1.1%. Since collagen contains only trace amounts of tryptophan, such analyses may be a convenient method for classifying proteins as collagens or keratins. R.M.L.

Occurrence of Collagen in the *Phylum Mollusca*. S. C. Melnick. *Nature*, **181**, 1483 (1958).

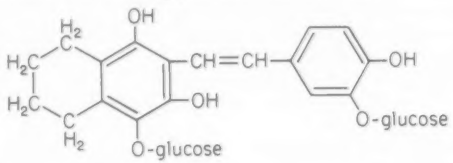
Molecular Weight of Condensed Tannins as a Factor Determining Their Affinity for Collagen. D. G. Roux. *Nature*, **181**, 1793–94 (1958).—A linear relation exists between the average molecular weight of such typical condensed tannins as black wattle and quebracho heartwood tannins and their R_M values [defined as log $(1/R_F\text{-}1)$]. This suggests the operation of physical forces between the tannins and cellulose or collagen. This is in line with increasing emphasis on the importance of van der Waals forces between cellulose and various solutes such as dyes. Tannin mechanisms are, however, exceptionally complex, and hydrogen bonding forces undoubtedly play an important part in the swelling of the hide, in the sorption and desorption of tannins, and possibly also in their fixation to collagen. R.M.L.

Rate of Swelling of Collagen. H. R. Elden. *Science*, **128**, 1624–25 (1958).—Due to the osmotic pressure gradient across the hide powder– solution interface, the fibrous matrix imbibes fluid with resultant volume increase. The concomitant decrease in entropy of the fibrous matrix produces a force which tends to resist further volume increase. The instantaneous velocity of swelling is related to the difference between the osmotic and entropic forces. An explicit relationship between volume and time is developed. R.M.L.

Quantitative Determination of Hydroxyproline by Paper Chromatography. H. R. Roberts and M. G. Kolor. *Nature*, **181**, 837 (1958).—A ninhydrin-isatin-triethylamine reagent offers the following advantages: it is specific for hydroxyproline; it is more sensitive than isatin; the maximum densities of the hydroxyproline color spots are greater and can be read immediately after color development. **A Rapid Chromatographic Procedure for the Quantitative Determination of Hydroxyproline.** H. R. Roberts, M. G. Kolor, and W. Bucek. *Ibid.*, **182**, 1602 (1958).—While the first method required 40 hr. for development, horizontal paper chromatography at 60°C. permitted reduction of the time to 4 hr. The standard deviation of the results was 2.21 mg. per 100 ml. R.M.L.

A Yellow Fluorescent Pigment in Elastin. F. J. Loomeijer. *Nature*, **182**, 182–83 (1958).—A yellow fluorescent pigment has been isolated from the elastin of *ligamentum nuchae;* this pigment is insoluble in water and petroleum ether but soluble in methanol, ether, and chloroform. The results of studies to date suggest a structure related to the pyrimidines, purine, or pteridines. R.M.L.

Spruce Bark Tannin. W. Grassmann. *Das Leder*, **9**, 193–202 (1958).—A review with 36 references. See also Endres, *JALCA*, **53**, 645 (1958). The following 5 tannin components in pure crystalline form have now been separated from spruce bark: (1) Picea-tannol with one double bond; (2) Dihydropicea-tannol in which the double bond has been hydrogenated; (3) a diglycoside of (1); (4) a monoglycoside of (1); and (5) a monoglycoside of (2). These components represent about 2/3 of the ethyl acetate fraction and about half of the alcohol fraction, and therefore approximately 35% of the total tannin and 7% of the inner bark. It has been shown that all 5 oxygens are phenolic. The tannin molecule has one double bond, and the strong shift in ultraviolet maximum on hydrogenation shows that it is in conjugation with the ring double bonds, indicating a stilbene arrangement. Splitting the tannin with cold permanganate produced 3 products, one of which was protocatechuic acid. The other two products were a split acid and a split phenol, each of which was oxidized to adipic acid by concentrated HNO_3. The phenol gave a green color with $FeCl_3$ showing that two of the hydroxyls were adjacent but not the third. From the various reactions and behavior of the tannin the following structure for the diglycoside was derived:



The aglucone (picea-tannol) was a good tanning agent, but the monoglycoside was a poor one. The tan and combining values of picea-tannol were 21.3 and 18.0, of dihydropicea-tannol 18.0 and 17.5, and of the monoglycoside 14.0 and 10.1 resp. Because most of the tannin in spruce bark is in the form of the glycoside, which has poor tanning ability, the slow enzymatic splitting

off of sugar in the tan liquors or pits plays an important role in the tanning process. The main tanning agent, however, is not the low-molecular aglucone but rather the more highly condensed products that are still soluble in water. The isolation of pure compounds has made possible improved studies of phlobaphene formation and sulfiting. Neither picea-tannol nor its glycoside was altered by heating with sulfite. When heated with dilute HCl picea-tannol darkened, and 90% of it precipitated. The precipitate was not soluble in water or the usual organic solvents and was not visibly altered by heating with a sulfite-bisulfite mixture. Brown, insoluble phlobaphenes were formed by oxidation of the tannin in the presence of the bark enzyme; one mole of picea-tannol took up one mole of oxygen. Intermediate oxidation products could not be isolated on a polyamide column because they could not be elutriated, but an intense red intermediate product, assumed to be a quinone, was formed by oxidation with $K_3Fe(CN)_6$ at pH 4.5–5.0. It was stable for several hours at pH 5, but at higher pH values it browned rapidly and precipitated as phlobaphene. In solution in ethyl acetate it was reduced rapidly to the original picea-tannol by free H_2SO_3 acid, but with Na_2SO_3 in the cold it was at once decolorized and sulfited to an anionic product that was soluble in water but not in ethyl acetate. A phlobaphene formed in the quinone solution on standing. When heated with a sulfite-bisulfite mixture, 80% of this phlobaphene dissolved in 30 min. The quinone was fixed irreversibly in a polyamide column and could not be eluted with dimethylformamide, the most powerful agent available. With pure products free from polyuronides, it should be possible to clarify the question of the tanning ability of sulfited materials. As an example, bark was extracted at 50°–60°C. with dimethylformamide, the liquor was evaporated to dryness, and the residue was heated with 80°C. water to obtain an extract of purity 70 and amounting to 9.5% of the bark weight. The water-insoluble portion was sulfited at 80°C., and an extract of purity 85 was obtained (equal to 6.5% of bark weight) that contained 1 sulfo group per 3 picea-tannol residues. It had a high affinity for hide powder and polyamide. I.D.C.

BOOK REVIEWS

Der Gerber in der Kunst. J. A. Sagoschen and F. Kirnbauer. Vienna: Verein Österreichischer Ledertechniker (VÖLT), 1958; 75 pp. 45 illus.—"The Tanner in Art" is the third in a series of cultural publications sponsored by the energetic director of the Viennese "Versuchsanstalt" for the Leather Industry, Prof. J. A. Sagoschen. Tanning—often called an art—has not made a very deep impression in the arts. Between Egyptian drawings and Renaissance woodcuts a wide gap remains to be filled. The "Tanner at the Beam" in the window of the famous Cathedral of Chartres is the only illustration of medieval origin. More fascinating for us moderns are the fine reproductions of paintings and of graphic art commissioned by Austrian tanners which have as their subject either the hand operations surviving in smaller tanneries or the enormous machine park of the "giants".

The authors are deeply conscious of the fact that theirs is a first attempt to collect material not of a pictorial history of tanning but works of art with tanning as subject matter. The reader is asked to lend his support by sending material to the VÖLT secretary, 79 Rosensteingasse, Vienna XVII.

L. SELIGSBERGER

Skin, Hide and Leather Defects. Jean J. Tancous, William T. Roddy, Fred O'Flaherty. Distributed by the Tanners' Council Laboratory, University of Cincinnati, Cincinnati 21, Ohio. $4.00—A quick examination of this book indicates that it is encyclopedic in subject matter and international in scope. In 10 chapters the text describes the following: 16 natural characteristics of hides and skins and their influence on the quality or appearance of the resulting leathers; 24 animal diseases encountered in living animals and the subsequent skin defects; the etiology and, in some instances, the life cycle for 7 parasitic infections in the living skin; 13 forms of careless mechanical handling of the living animal which result in skin damages; 11 skin defects which have their origin in the slaughterhouse; 38 forms of damage attributed to malpractices in the curing, storage, and shipping of hides and skins; 20 causes of skin damage that are assessed against beamhouse processing; 18 poor conditions encountered in the pickling, degreasing, and tanning operations; 8 defects resulting from leather-finishing operations, or damages from earlier plant operations that show up in the finishing department; and finally a group of 10 defects and/or damages incurred during storage of finished leathers or in-service failures.

The value of this book is greatly enhanced through the generous use of photographs as examples of the many subjects under discussion. Grouped together as one chapter are 68 photomicrographs which show with great clarity how the structure of the hide or skin is either permanently altered or otherwise involved through disease or by some form of malpractice in the transition from raw material to finished leather. There is ample evidence to show that the intelligent application of microscopy in the field of leather processing is a very useful and proven instrument. To round out this book the final chapter presents some discussion of, and directions for, histological techniques which the authors have found most useful in investigation by microscopical methods of the numerous aspects of skin damages and defects. The fundamental correlation of the book suggests that the success of the final product is largely dependent upon the physical state of its structural elements.

A comprehensive literature search is evident in the 221 references given, and the authors have effectively used this information to augment and support their own extensive experience in "trouble-shooting." The purpose of the book, as stated in the Introduction, is to "provide a basis for the identity of the defects and to suggest means of identifying and eliminating these serious economic losses which result in devaluating leather." In this respect the objective is fully attained, but it is not within the scope of the book to proffer complete remedies, since it is more within the province of the individual tanner or leather processor to achieve his own balance of operations.

The organization of the material, the clarity of the illustrations, and the printing combine to make this a ready reference source of considerable value to the cattle breeder, the packing-house man, the tanner, and the leather processor alike.

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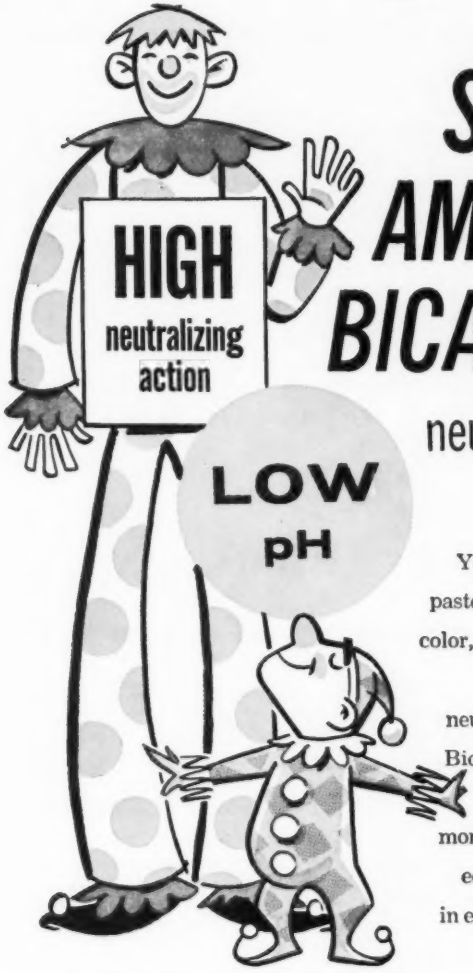

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Your inquiries will be gladly answered.

Address DR. FRED O'FLAHERTY, Director
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